











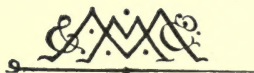




CRYSTALLOGRAPHY

AND

PRACTICAL CRYSTAL MEASUREMENT



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# CRYSTALLOGRAPHY

AND

## PRACTICAL CRYSTAL MEASUREMENT

BY

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PAST PRESIDENT OF THE MINERALOGICAL SOCIETY

IN TWO VOLUMES

VOL. I

FORM AND STRUCTURE

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## PREFACE TO SECOND EDITION

THE subject of Crystallography has made such remarkable progress since the year 1911, when the first edition of this book was sent to press, that a new edition is urgently called for. The startling discovery of Prof. von Laue, that the planes of atoms in a crystal are capable of reflecting and diffracting X-rays, and thereby of revealing the inner structure of the crystal, was only made in Munich in the year 1912, a year after the book was published; and the masterly development of this mode of attack on crystal structure by Profs. Sir W. H. and W. L. Bragg, together with the contributions of quite a number of other workers attracted to so novel a research, has rendered the last nine years a period of epoch-making progress, in spite of the Great War which has absorbed so much scientific energy. The present is a particularly suitable moment for recording in a second edition the results achieved, and an entire new chapter of considerable length has been added to embody them, besides many other references scattered throughout the book. For a new light has been shed on crystallography by this exceptionally interesting and far-reaching method of investigation, and the most satisfactory fact about it is that X-ray analysis has not only fully confirmed all the main conclusions as to crystal structure which were detailed in the first edition, but has rendered them now incontrovertible. It is most inspiring that the principles which have been established by many years of hard work on the part of crystallographers and geometricians should now receive such absolute confirmation in so unexpected a manner. For not one single conclusion or principle, presented in the first edition, has been shown to be invalid or incorrect.

Our conceptions of the arrangement of the constituent atoms in crystallised solid substances, as occurring on the lines of the 230 types of homogeneous structures based on the fundamental 14 space-lattices, and which are in agreement with all the results of crystal measurements as described in the first edition, are now definitely proved by the X-ray analytical results to represent the truth. The atoms which we knew must be there, and in the positions which we imagined, are now actually located *in situ* and their distances of separation from one another determined in absolute measure. The very dimensions of the space-lattice cells, which in some cases of strictly isomorphous substances we had

ventured to fix in relative measure, are now proved to possess absolute values bearing precisely those relations. Consequently, X-ray analysis has given an immense stimulus and incentive to still further research into the secrets which crystals yet hold in store for the earnest seeker after truth and new knowledge, a fact which is especially cheering to those whose work is thus so happily confirmed.

Besides the new chapter concerning X-rays and crystal structure, four other new chapters have been added, largely in response to many requests. In the anxiety not to render the book too large for a single volume, the scope of the first edition was purposely restricted. But the desirability now, after the lessons taught by the War, of giving to English-speaking students and investigators, in their own language, both in the British Empire and America, as complete and yet concise an account of the subject as possible, has overborne this consideration, and new chapters have been added on (1) Isomorphism, (2) Polymorphism, Isogonism, and Enantiomorphism, (3) the Thermal Properties of Crystals (additional to dilatation which was already fully dealt with), and (4) the Electrical and Magnetic Properties of Crystals. The author cannot express his thanks to his critical and often very helpful reviewers too warmly; besides these new chapters which they recommended it has been found possible to attend to every one of their valid criticisms, to include some account of everything that was specified in the reviews as wanting in the first edition, and to correct every misstatement or slight inaccuracy to which attention was called.

Among the more noteworthy additions may be mentioned (1) a very considerable expansion of the chapter on two- and three-circle goniometry, and on the use of the gnomonic projection; (2) an illustrated account, for the benefit especially of workers with X-rays, of each of the 65 regular point-systems of Sohncke, and the evolution therefrom of the remaining 165 of the 230 types of possible crystal structure; (3) a considerable enlargement of the chapter on microscopical methods of dealing with small crystals, whether alone or in rock sections; (4) a summary of the magnificent recent work on the structure of the atom, an account of Moseley's law connecting atomic structure with atomic number, which so wonderfully and logically explains the author's own law of progression of the crystal properties in isomorphous series, an epitome of the latest facts concerning radioactivity and the nature of X-rays, and an account of the remarkable revelation of isotopic forms of many of the chemical elements, including the latest discoveries of Dr. F. W. Aston by means of his positive ray mass spectrograph, all of which are essential to a thorough understanding of the true nature of the perfect solid, a crystal, and of the new avenues of research open to crystallographers.

Other less lengthy additions refer to goniometry at very high and very low temperatures, the luminescence of crystals, their absorption of light including an account of absorption brushes, surface colour, pleochroic haloes, optical anomalies, asterism, crystal viscosity and its relation to the remarkable properties of ice, the foam and pulsation cell theories,



“liquid crystals” and the swarm theory, the determination of the torsion of crystals by an interferometric method, and further crystallographic use of the principles of interferometry, and their application not only in the author’s own methods but in those of Michelson and of Fabry and Perot. Five new plates have also been added, bringing the total number of half-tone plates up to eight.

The book is bound in two volumes, the first of which deals with Crystal Form and Structure, and the second with the Physical and Chemical Properties of Crystals. A rearrangement of some of the chapters among themselves has also been effected which, with the additional chapters logically placed, enables the book to be divided into four parts, each more or less complete in itself. These four Parts are: I. Crystal Form and Goniometry; II. Crystal Structure and its X-ray Analysis; III. Crystal Optics and Microscopy; and IV. Crystal Chemistry, Deformational Physics and its Interferometry. Parts I. and II. constitute the first volume, and Parts III. and IV. the second volume. It is hoped that by this course the book may attain to a maximum of convenience and usefulness in assisting the study of the subject of Crystallography, now so greatly enhanced in value and importance, and appealing to so much wider a circle of readers and investigators.

The present book also includes the whole of the material and illustrations of the author’s monograph *Crystalline Structure and Chemical Constitution*, which is now out of print, and brings the conclusions arrived at in that work right up to date.

The author is especially indebted to Sir William Bragg and to Prof. W. L. Bragg for the quite exceptionally kind manner in which they have supplied the author with their very latest X-ray results, right up to the time of the revision of the final proofs in April 1921, and for full facilities afforded throughout for the effective illustration of their apparatus and results by original figures. The author is also under deep obligation to Lord Rayleigh, Sir Henry Miers, Dr. Arthur Hutchinson, Dr. Herbert Smith, Prof. von Laue of Zurich, Prof. Jaeger of Groningen, Miss Mary Porter, Prof. Bowman, Mr. T. V. Barker of Oxford, Mr. Twyman of Messrs. Hilger, the Royal Society, the Royal Institution, the Royal Society of Arts, Messrs. G. Bell & Sons, and to Messrs. Kegan Paul & Co., the publishers of the author’s *Crystals*, for their kindness in supplying electros and materials for illustrations or the text, which have greatly added to the value and interest of the book; and not least to the engraver, Mr. Frank Butterworth, who has taken such infinite pains to render the details of the large number of new figures accurate to the utmost degree. To Messrs. Macmillan, for undertaking the publication of so considerably enhanced a work at a time of peculiar difficulty and expense, the author is indebted more than he can ever express. Their action can only be regarded as a direct contribution to the advancement of Pure Science.

A. E. H. TUTTON.





## PREFACE TO FIRST EDITION

IN this book an endeavour has been made to present at the same time both a guide to practical work in crystallography and all the essential theory of the subject, not only as regards crystal morphology but also with respect to the physical properties of crystals. The aim has been to give the main facts unencumbered with obsolete nomenclature, notation, and methods, which confuse and discourage the student or enquiring reader, and occupy time that could with greater advantage be spent in acquiring familiarity with the goniometer and a knowledge of facts of real use in the practical experimental investigation of crystals.

For this reason the notation of Naumann for the labelling of crystal faces is discarded for the more scientifically founded method of Miller, which is in harmony with the important recent development and completion of the geometrical theory of crystal structure, and regards crystals as homogeneous structures built up by the arrangement of their chemical molecules, and the atoms of which they are composed, according to definite schemes of symmetry. For the same reason the conceptions of hemihedrism and tetartohedrism are eliminated in favour of the now well-established principle, that the various classes of the same system of symmetry are different entirely because they possess in a definite manner more or less of the elements of symmetry (planes and axes of symmetry) possible to the system, in various stages and modes of combination, from the class possessing the minimum essential elements of the system to that endowed with the maximum number.

Another feature of the book is that the forbiddingly mathematical aspect of so many works on crystallography has been altogether avoided; the student is shown that there are really no mathematical difficulties involved, but that, on the contrary, all the necessary calculations of crystal angles and elements, as well as of the physical constants, are both simple and straightforward, requiring only an ordinary acquaintance with simple trigonometry and the use of a table of logarithms. Four pages only of mathematical instructions and formulæ, given in Chapter VII., form the key to all the morphological calculations required.

The practical use of the goniometer, which at once clears away all preconceived difficulties, is taught from the very beginning of the book, immediately after the necessary instructions for selecting or preparing

crystals for goniometrical purposes have been given. A typical crystal is measured as early as Chapter IV., and from the actual observations made with it all the salient fundamental facts of crystal morphology are discovered in their natural sequence, thus leading up to their systematic consideration in subsequent chapters.

The method adopted in this succeeding part of the book has then been to give first a chapter on the symmetry of the crystal system under consideration, and to follow it immediately with another in which a characteristic well-formed crystal of a substance crystallising in that system is actually worked through on the goniometer; indeed in the cases of several of the systems two such crystals of substances belonging to different classes of the system are thus employed as practical typical examples. In all cases these are chosen either from readily procurable minerals and such as form small well-developed crystals suitable for goniometry, or from easily prepared chemical salts known to afford good crystals without difficulty. From these practical measurements in each case the symmetry is deduced, the stereographic and clinographic projections of the crystal are accurately drawn, the crystal elements and angles are calculated from the best measured basal angles, and the results are expressed in the approved tabular form, precisely as if for publication.

In one of these cases—the measurement of copper sulphate as an example of triclinic symmetry in Chapter XX.—the whole chapter is really a record of an original investigation now published for the first time; for the existing data concerning the crystallography of copper sulphate are so confused that a reinvestigation was imperative. The student is thus enabled to follow an actual piece of research through all its stages.

The fact that no two crystals are ever alike entirely saves this method from being a cut-and-dried one, affording no opportunity for original thought and treatment. For the crystals of suitable small size and perfection, purchased from the mineral dealer, or grown in the laboratory by the student personally, with the object of repeating the measurements here detailed and working through the chapter practically with the goniometer, while being similar can never be copies, and will generally afford some additional or different faces, or be deficient in others, compared with those exhibited by the crystal described in this book as typical of the substance.

A special endeavour has been made in Chapter IX. to give a full but concise account of the important work on the geometrical theory of homogeneous crystal structures, and in Chapter XXXI. of the development of the fruitful idea of molecular distance ratios, the dimensions along the three axial directions in space of the elementary cell (the habitat of a molecule) of the space-lattice of the crystal structure, our nearest approach to the determination of the molecular dimensions. Practical guidance is also given in the succeeding chapter for the determination of the density of crystals, now in consequence rendered so very important.

The illustrations are almost entirely original and of two kinds, namely, (1) direct reproductions of the author's own drawings, which include all



the figures of crystals, and (2) wood-cut engravings; the latter are used to illustrate every instrument and piece of apparatus referred to in the text, a large number of which are in the author's own laboratory. The drawings of crystals have all been constructed to scale and according to the axial ratios and angular elements of actual substances, the very few copies of crystal forms being taken with full references and acknowledgments from the memoirs of original authors. Besides the essential instruction in clinographic projection given in Chapter XXV., the great utility of the stereographic projection, on the lines indicated by Penfield, as an important aid to the drawing of crystals, has been emphasised. The illustrations of interference figures afforded by crystal plates in convergent polarised light are almost exclusively reproductions of actual photographs taken by the author.

An attempt has been made to render the optical portion of the book a special feature. So little practical aid has hitherto been forthcoming for the student in this domain of crystal optics, that it is no wonder the optical details are usually so meagre in the published descriptions of the crystals of new substances. The optical part of a crystallographic investigation is frequently of exceeding interest and often of prime importance, and it is hoped that a really practical guide to this branch of the work will be found in the book. Moreover, the science of optics has been undergoing such remarkable changes of recent years, owing to the rapid succession of discoveries of the first rank, that an introductory chapter (XXXIV.) has been given in which the present position of the theory of light is briefly presented, as a definite basis on which to rest the subsequent chapters applied to crystal optics.

The chapters on the microscope include a full account of the important new methods introduced by Becke and von Fedorow, and it is hoped that they will be a help in presenting the difficultly accessible work of these investigators to English readers. The chapters on the thermal expansion and elasticity of crystals are also of a fully practical character, and the instruments employed, which are mostly original, illustrated.

The last chapter (LV.) includes a brief account of the liquid crystals discovered by Lehmann, with instructions for their study by observation or screen projection.

The author desires to record his indebtedness to Principal Miers, F.R.S., for much kindly help and criticism, which has materially enhanced the value of the book, and for his permission to illustrate by new wood engravings the whole of the instruments designed by him. Also to his successor at Oxford, Professor Bowman, for similar facilities concerning his additions to the Oxford instruments. To Dr. Herbert Smith of the Mineralogical Department of the British Museum (Natural History) at South Kensington the author's best thanks are due, for like privileges in connection with the two three-circle goniometers with which he has enriched the science, as well as with respect to the total refractometer and other attributes of goniometrical-optical research on crystals which he has devised, and for the permission to redraw certain illustrations of his memoir concerning the gnomonic projection of crystals. To Dr.

Hutchinson of Cambridge the author is also indebted for the kind loan of the beautifully prepared copper engraving of his stereographic net, and of the blocks illustrating his stereographic protractor and his universal apparatus. Also the author's sincere thanks are due to Mr. T. V. Barker for most kind assistance in presenting the work of Professor von Fedorow, with whom he studied in St. Petersburg, adequately before the readers of this book. For much kindly help and many valuable suggestions in connection with the geometrical theory of crystal structure (Chapter IX.), and with the valency theory of Pope and Barlow (Chapter XXXIII.), the author is deeply indebted to Mr. W. Barlow, F.R.S. The author also desires to record his hearty thanks to the firm of Carl Zeiss, for kindly placing at his disposal for experimental demonstration their beautiful apparatus for the study of liquid crystals, together with facilities for preparing a wood engraving of the heating microscope employed. Similarly, to Messrs. Swift for the loan of electros of certain attributes of the Dick microscope, and for facilities for illustrating this beautiful instrument in its absolutely latest form with a new wood engraving. Also the author is particularly desirous of recording his thanks to the firm of Steeg and Reuter of Homburg, for very kind help in obtaining suitable sections of mineral crystals for the preparation of the photographs of interference figures, and for the loan of electros of their well-known sectioning apparatus.

The author cannot conclude without paying a tribute to the careful work of the engraver, Mr. Frank Butterworth, to whose personal skill and draughtsmanship it is due that the wood engravings of this book are such faithful representations to the last details of the most recent form of crystallographic instruments. The author also wishes to express in conclusion his gratitude to Messrs. Macmillan for their unfailing kindness and consideration during the production of the book, and particularly for their public-spirited expenditure on a work of this kind, which can scarcely hope for a very wide circulation in the early days of this growing science of crystallography, when its value is only just beginning to be realised. That there is a great future before this subject, the science of the organised and perfect solid, is assured, however, and that the book may help forward the progress of crystallography by enabling it to be more widely studied, and its value to be more fully appreciated, and especially that there may be attracted to it an increasing number of earnest spirits seeking for a field of fascinating and richly rewarding research, is the author's chief aim and desire concerning it.

A. E. H. TUTTON.

The Chapters referred to in this Preface to the First Edition as IX., XX., XXXIII., XXXIV., and LV. are now in this Second Edition Chapters XXX., XIX., XXXIV., XXXV., and LX. respectively.

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PART I

CRYSTAL FORM AND GONIOMETRY





*“Quare sexangulis nascatur lateribus non facile ratio inveniri potest; eo magis quod neque mucronis eadem species est, et ita absolutus est laterum laevor, ut nulla id arte possit aequari.”*

*Natural History of Pliny, Book xxxvii. 9.*

## CHAPTER I

### THE NATURE OF CRYSTALS

A CRYSTAL is solid matter in its most perfectly developed and naturally organised condition. It is characterised by an exterior form of extraordinarily regular geometrical design, carried out much more accurately than can be attained by artificial construction, except by great expenditure of time and rarely attained skill; also by an internal structure of a nature likewise so regular that the arrangement of the ultimate particles or structural units, which are in general the chemical molecules or small groups of molecules, about any one point in the structure is precisely the same as about every other point. If the growth of the crystal has been slow, undisturbed, and unrestricted in all directions, its external shape is that of a closed solid the surface of which is entirely made up of numerous truly plane facets, technically termed “faces,” meeting in straight edges, brilliantly smooth as if highly polished, and the arrangement of which with respect to each other, as measured by their mutual inclinations, is characteristic of the particular substance of which the crystal is composed (unless the crystal belong to the cubic system, when the perfect symmetry fixes the angles). The appearance of such a perfect crystal is shown in Fig. 1, which represents a crystal of the common substance, sulphate of potash,  $K_2SO_4$ . “Crystal” is the Anglicised Greek word for “ice,” frozen water, namely, *κρύσταλλος*. It was employed also in the Middle Ages to designate rock-crystal (quartz), which was considered (by Albertus Magnus, for instance, in the year 1250) to be a form of ice hardened by the Alpine cold. The term has thus come to include crystals in general, and knowledge concerning crystals to be the science of Crystallography. So long ago even as the first century A.D. many of the more interesting external properties of natural crystals had been observed. For it is obvious that Pliny, the elder, in the interesting statement (date about A.D. 77) in his *Natural History* above quoted, is referring to rock-crystal (quartz),

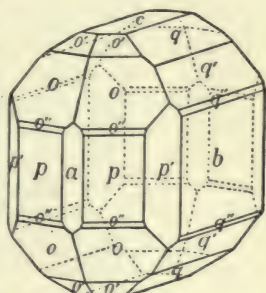


FIG. 1.—Potassium Sulphate Crystal.

and that he had remarked the hexagonal prismatic form (see Figs. 311 and 312, Chapter XXII.) of the crystals, and found it difficult to account for such regularity of form, and particularly for the varied appearance of the pyramidally-pointed ends; he had also noticed the wonderful polish of the prism faces, which he considered to be such as no man could equal. Pliny's Book xxxvii., in which this statement occurs, is the last volume of his celebrated *Natural History*, and is devoted to Precious Stones. It was published only two years before his natural curiosity caused his death in the fumes from Vesuvius during the great eruption of A.D. 79, when Pompeii was destroyed.

It will be observed that in the definition given in the first paragraph a crystal is regarded as a solid, and the crystals employed for the purposes of measurement, both of angles and of optical and other physical constants, must obviously be such, although they may vary in hardness from that of the diamond down to that of gypsum and of the softer chemical salts and preparations. A most interesting borderland between the softest of crystals, as we ordinarily know them, and liquids, has been brought to our notice during the last twenty years, however, by the brilliant investigations of Lehmann concerning certain viscous organic liquid substances and even mobile oils, which he has shown possess the property of double refraction and the power of definite orientation of their molecules in organised assemblages which he terms "liquid crystals." Keen controversy has been excited as to the suitability or otherwise of this term, which on the whole would appear to be misapplied, and over the theoretical deductions of Lehmann. An account of these remarkable substances will be given in the last Chapter, LX. of this book, and it will be shown that the definition of a crystal does not require to be modified on their account; for these so-called "liquid crystals" are not truly crystals, and are therefore not competent to be included in the scope of the definition.

**Faces of Crystals perfectly True Planes.**—In referring to the faces as being truly plane, it is not merely meant that they are as flat and highly polished as the facets imparted to a precious stone by the jeweller's lapidary, but that they are optically true planes, as perfectly even as those surfaces which the most highly skilled opticians can only produce by days and often weeks of most patient labour. The result is that perfect natural crystal faces reflect light like a mirror, and the reflections which they afford of surrounding objects resemble those objects as truly as in the case of the optically worked reflecting surfaces just referred to. Moreover, this is true whether the substance of the crystal be opaque or transparent. If the latter, then part of the light only is reflected, the amount depending on the angle of incidence, being least for perpendicular incidence, but anyhow ample to afford excellent images. The other part penetrates the substance of the crystal, and suffers dispersive refraction in accordance with the well-known laws of refraction, more or less modified if the crystal belong to any other system of symmetry than the cubic. Further, on reaching the faces on the other side of the crystal the dispersed rays may partially pass out, and partially be reflected back again in accordance with the ordinary law of reflection at a transparent



surface, or they may be internally totally-reflected, provided the angle of incidence on one or more of the back faces is greater than the so-called critical angle, the whole of the light incident on that face or those faces being then totally-reflected, in accordance with the optical law of total-reflection which governs what occurs on an attempted passage from a more highly (in this case the crystal) to a less highly (the air) refractive medium.

It is to this latter fact that is due one of the most beautiful properties of transparent crystals, namely, the scintillation of spectrum-coloured rays when the crystal is viewed in sunshine or a bright artificial light, which causes so many of the harder and more durable of naturally occurring crystals, such as the diamond, sapphire, ruby, and emerald, to be so highly valued as jewels and gem-stones. A diamond (which possesses the perfect cubic symmetry), provided with numerous cut and polished facets for use as a brilliant (as unfortunately the natural faces of the diamond have usually been rounded by corrosion), exhibits the phenomenon to perfection; for owing to the very high refractive power of diamond, and its exceptionally great dispersion (long spectrum), almost all the light which penetrates the crystal, namely, all which internally meets any face or facet at any angle greater than  $24^{\circ} 13'$ , suffers internal reflection before being permitted eventually to emerge in brilliant spectrum colours from the crystal.

The high order of reflection from crystal faces is the foundation of practical crystallography, for upon it is based the use of the chief instrument of the crystallographer's laboratory, the reflecting goniometer, with the aid of which the angles between the crystal faces are measured. The crystals found in nature, or prepared by the usual artificial means (deposition from a saturated solution of the substance in a solvent, cooling of the fused substance, or condensation of the vaporised substance), only more or less rarely exhibit the state of perfection described in the opening paragraphs. But sooner or later such perfect crystals are met with naturally, or are obtained by careful preparation, in the case of crystallisation from solution by taking precautions to avoid rapid changes of temperature, concussion, or other brusque disturbance of the solution during the period of deposition of the crystals. It amply repays to take such precautions, and to select carefully only the very best crystals for measurement on the goniometer, for the results are far more valuable than the mean results of a very large number of measurements with inferior crystals.

**The Constancy of Crystal Angles.**—The fact that the crystalline form is the most distinctive and characteristic property of a solid substance, offering the most infallible evidence of its identity, would alone suffice to render crystal measurement of the highest importance. By "crystalline form," however, is not meant the relative extent of development of the different faces, but the arrangement of those faces, as defined by the geometrical angles between them. To render this clearer, illustrations of two other crystals of the same substance which is represented in Fig. 1, potassium sulphate, are given in Figs. 2 and 3. Precisely the same faces

are present in all three cases, but their relative development is so different that the crystals would appear at first sight to have no single point of similarity. It was this great diversity of appearance, consequent on great variety displayed in the development of the faces of the crystals of one and the same substance, that had puzzled Pliny so especially, and, in times more nearly approaching our own, that for so many years delayed the acceptance of the conclusion published by the Abbé Haüy in the year 1784, that every substance of definite chemical composition is distinguished by its own particular crystalline form. In the case of potassium sulphate actual measurements of the angles between any analogous well-developed pair of adjacent faces on the three crystals represented in the figures, which were particularly good crystals employed in the author's research on the alkali sulphates, showed that in every case they were identical to within two minutes of arc. Another striking example of the difference of form development displayed by crystals of the same substance, this time taken from naturally occurring mineral

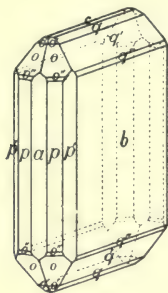


FIG. 2.

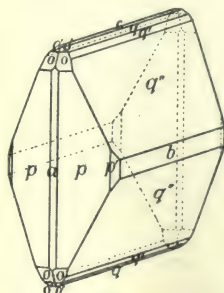


FIG. 3.

Two further Types of Potassium Sulphate Crystals.

crystals, is illustrated in Figs. 4 and 5, which represent crystals of calcite from the same mine, the Bigrigg mine at Egremont, Cumberland. The specimen portrayed in Fig. 4 is one of the well-known "dog-tooth spar" exhibiting predominatingly the scalenohedral habit of calcite; whilst that represented in Fig. 5 consists of hexagonal prisms capped by low rhombohedra. Yet the same hexagonal prism is present also on the crystals of Fig. 4, the scalenohedra forming their terminations, and all three forms are those characteristic of calcite (and of class 21 of the trigonal system), and are commonly found, all three present together, on crystals of calcite.

This constancy of the interfacial angles, so excellently illustrated in the specific cases of potassium sulphate and calcite, is a general law of nature, as regards the crystals of any one definite substance, and the law forms the corner-stone of the science of crystallography. It was first announced in a dissertation, *De solido intra solidum naturaliter contento* (printed in Florence, where Steno resided for a time), of the year 1669, by Nicolaus Steno—Professor of Anatomy at the University of

Copenhagen, Vicar Apostolic of the North, who was also both a geologist and palæontologist—as the result of rough measurements (no accurate instrument being then invented) made on specimens of rock-crystal (quartz) from different localities. It was confirmed in two memoirs of



FIG. 4.—“ Dog-tooth Spar ” Calcite.



FIG. 5.—Prismatic Calcite.

1688 and 1705 by Guglielmini as being a general law of nature. Romé de l'Isle<sup>1</sup> in Paris in 1783, using the contact goniometer invented by his assistant Carangeot in 1780, gave the law greater accuracy, and paved the way for the important work of Haüy published in 1784.

<sup>1</sup> Born 1736, died 1790. His celebrated *Essai de cristallographie* was first published in 1772, and republished in enlarged form in 1783 under the title *Cristallographie ou Description des formes propres à tout les corps du règne minéral*. The latter work included figures of more than 500 crystal forms.



**Final Proof of Angular Constancy and Individuality even in Cases of Extreme Similarity.**—Yet the perfect truth of this fundamental law has only quite recently been fully proved. For the principle of “isomorphism,” discovered in the year 1819 by Mitscherlich, implied, as indicated by the term used to designate it, that certain series of similarly constituted substances,—such for instance as the numerous well-known series of chemical salts in which the metal present may be replaced by any other metal of the same family group,—possessed identical crystalline forms. Although Mitscherlich himself was subsequently of opinion that only similarity and not identity of form obtained in these cases, the published measurements of the crystals of the members of such series were so conflicting until so late as the year 1890 that it was impossible on existing data definitely to decide the question. Since the year just mentioned, however, the author has carried out an organised series of investigations, having for their main object the settlement of this fundamental question, employing highly perfect crystals, prepared with very special care, of seventy-five salts belonging to five of the more important of these series crystallising in the rhombic and monoclinic systems (not cubic, as the perfect symmetry of this system admits of no variation of angles). The result has been to establish definitely the fact that relatively small but very real differences of angle do occur between the crystals of different members of any one series, and that each member of the series is thus characterised by its own distinctive angles. Further, the differences have been shown to be subject to a definite and very interesting law, namely, that they follow the order of the differences between the atomic weights or atomic numbers of the metals or other dominating interchangeable chemical elements which give rise to the series, so that the angles are functions of the atomic weights or atomic numbers. Indeed, the law is much more far-reaching than this, for it embraces in its scope not only the relations of the angles between the exterior faces, but also the whole of the internal as well as external, including the optical and thermal, properties of the crystals, all of which are also functions of the atomic weights and atomic numbers of the interchangeable elements. It has been stated by the author as follows: **The difference in the nature of the elements of the same family group, which is manifested in their regularly varying atomic weights and atomic sequence numbers, is also expressed in a similarly regular variation of the characters of the crystals of an isomorphous series of salts of which these elements are the interchangeable constituents.**

This generalisation, which is based on the indubitable result of many thousands of accurate measurements, finally disposes of all doubt as to the constancy of the crystal angles of any one and the same substance; it defines the limited sense in which Mitscherlich's law of isomorphism is true, thus reconciling the views, formerly considered antagonistic, of Haüy and Mitscherlich, and leaves as the expression of a fundamental truth the statement that: **To every solid crystallisable substance of definite chemical composition there corresponds a crystalline form which is proper and special to that substance, and by which the latter can be recognised and identified.**

The small interfacial angular differences observed in the cases of isomorphous series, which have been shown to be subject to the law of progression with the atomic weight and atomic number of the interchangeable chemical elements of the same family group which produce the series, increase with diminution of the symmetry, and diminish as the symmetry of the crystal increases, until, when the perfect symmetry of the cubic system is attained, they disappear altogether. For, as already mentioned, the angles of a cubic crystal are fixed by the symmetry, and are therefore invariable. In the case even of a cubic crystal, however, the optical, thermal, and other properties continue to obey the law. The differences of interfacial angle in these strictly isomorphous series rarely attain  $3^\circ$ , even in the lowest systems of symmetry.

## CHAPTER II

### THE PREPARATION AND SELECTION OF MEASURABLE CRYSTALS, AND THE NATURE OF THE PROCESS OF CRYSTALLISATION FROM SOLUTION

**The Size of Crystals for Measurement.**—The most suitable crystals for goniometrical measurement are usually of small size, somewhere between that of a pin's head and that of a pellet of small shot. For the minute faces of such crystals as a rule exhibit less distortion than larger ones. There are cases, however, of substances the faces of which habitually show such perfection of planeness that somewhat larger crystals, as much as three or four millimetres in diameter, or, in the case of elongated prismatic crystals, across their narrowest part, may be safely employed, but such instances are rare. On the other hand, discrimination requires to be used as to the acceptance of angular measurements from crystals of less than a millimetre diameter; for the images of the reference signal-slit of the goniometer, reflected by the smaller faces, which must obviously be very minute on such crystals, are relatively so much less brilliant that it is difficult to distinguish a simple perfect image, derived from a truly plane face, from the brightest of a bundle of images derived from a distorted or striated face, owing to the feeble illumination of the weaker subordinate images of the bundle, which may cause them to be overlooked. Hence, while very small crystals are generally preferable for measurement, discretion must be employed. As a rule, a crystal of an intermediate size between the dimensions just referred to will prove a happy choice.

**The Selection of Crystals of Minerals.**—In the case of mineral crystals it is only necessary to examine all the material available, and to select, with the aid of a pocket lens, those crystals which are of suitable size, in accordance with the above considerations, and which are obviously the best formed and endowed with faces apparently free from distortion or striation. It may be that several such will require to be tested on the goniometer itself, for every one that is finally chosen as fulfilling the desiderata.

**The Preparation of Crystals from Solutions.**—When the substance under investigation is a chemical compound which is crystallised, as is most frequently the case, from a solvent (usually water, but in cases of carbon compounds probably alcohol, ether, acetone, benzene or other organic liquid), a number of different crops of crystals should be prepared.



The solutions are preferably placed in small flat-bottomed glass beakers or thin glass crystallising dishes, all scrupulously clean, and every possible precaution must be taken against draughts of air or other cause of rapid change of temperature, against mechanical disturbance of any description whatsoever, and particularly against the intrusion of dust. The crystallising vessels should rest on felt, and the latter on wood, the wooden top of the working bench or table being quite suitable, provided all metal or other good conductors are removed, and non-conducting screens are placed so as to surround the felt-covered part. The room should be a quiet one, free from dust and not liable to sudden change of temperature. For the obvious reason that a large room can rarely be given up for the purpose, it is preferable to set apart a small room for the crystallisation, or at any rate to reserve a quiet corner for this all-important work.

It is usually unwise to crystallise by cooling from strongly supersaturated solutions, as the crystals then form so rapidly that they are generally distorted, or acicular, or otherwise unsuitable for measurement. The best course is to prepare a hot solution not quite saturated. If there be the slightest deposit in the solution it should be filtered, and the clear liquid allowed to fall directly into the several small crystallising dishes or beakers to be employed, and to the extent of not more than an inch deep in each. The beakers ought to be first warmed, as a very cold beaker may start crystallisation at once. During cooling to the ordinary temperature there will be some evaporation of the solvent, with the production of a solution which will be more or less supersaturated by the time the atmospheric temperature is reached, according to the amount of evaporation and to the difference in solubility of the substance at the boiling temperature of the solvent and at the atmospheric temperature. As a rule crystallisation will supervene during the succeeding night, and next morning a crop of apparently well-developed crystals will be found, at any rate in one or more of the beakers. A little experience with the substance under investigation will soon teach one the best conditions for crystallisation, and they will vary for different substances as considerably as do the solubilities of those substances. The rules just given, however, will be found to be of very general application. They will be further developed and explained later in this chapter (see pages 24 and 25), after discussing the nature of, and the exact conditions for, solubility and supersolubility.

**Removal and Storage of the Crystals.**—Having thus secured one or several such crops the crystals should be taken out, as early in the morning as is convenient; for otherwise the normal rise of the atmospheric temperature with the altitude of the sun will warm the mother liquor sufficiently to round the edges of the crystals, owing to the solubility being usually greater the higher the temperature. The removal is best effected by decanting off the mother liquor (the technical term used to designate the solution standing over deposited crystals) into another clean beaker, which had better be first warmed. The clear liquid in this second beaker may then be advantageously brought just to boiling over a very small flame of the Bunsen gas burner, and the beaker set aside



for the production of a second crop on the succeeding night. The crystals left in the first beaker may then be gently removed and placed on a double sheet of clean white blotting- or filter-paper to drain. They should next be moved about over the sheet by several small strips of blotting-paper in succession, until free from traces of mother liquor, and be eventually transferred to a fresh sheet of blotting-paper and allowed to dry completely in ordinary dry air, assuming that the substance is not hygroscopic. When, however, the substance is a deliquescent one (absorbing moisture from the air), the paper and crystals must be placed in a desiccator containing concentrated sulphuric acid, calcium chloride, phosphoric anhydride, or other powerful absorbent of water vapour, to dry.

Each crop of crystals thus obtained should be stored in a separate small bottle, labelled with the name or chemical formula of the substance and the date of collection of the crop. The contents of each can then be separately examined for crystals of suitable size and the required perfection of faces for use in the measurements, and any peculiarities of habit on the part of the crystals of that particular crop studied.

**Procedure in the Case of very Deliquescent Crystals.**—In the case of the crystallisation of very deliquescent substances during damp weather, it is frequently advisable, and sometimes necessary, to place the crystallising vessels inside the receiver of an air-pump, along with the usual desiccating dish of sulphuric acid, or, in extreme cases, of phosphoric oxide, and to reduce the pressure of the air within the receiver, by means of the pump, to something less than one-third of the outside atmospheric pressure. The progress of the crystallisation requires in this case to be carefully observed every few hours, as otherwise the crystals may grow to too large a size.

A very convenient form of desiccator for use either at the ordinary or under reduced pressure, is that of which a battery of six is shown in Fig. 6. It is simple, and never gets out of order or collapses at a low interior pressure, as some of the more elaborate vacuum receivers are apt to do. A strong glass bell-jar, with ground tubular open neck and ground lower rim, rests by the latter on a slab of plate glass also ground. The neck is closed by a good indiarubber stopper, of such size and taper that the exterior atmospheric pressure is incapable of forcing it through the neck, and perforated by a single hole through which there just passes a short glass tube bent at right angles, having a well-fitting stopcock blown on the vertical limb. The fitting of the truly plane rim of the bell-jar on the slab, of the caoutchouc stopper in the neck, and of the stopcock in its tubulure on the short tube, is in each case rendered airtight by a thin film of pure vaseline. It is a great mistake to use cerate or other wax, as this is no substitute for well-fitting glass grinding, and it is not only a poorer closing medium but also, owing to its hardening, gives infinite trouble on again opening the receiver, generally causing upsetting of the crystallising vessels or derangement of the crystals exposed on filter-paper for drying. If the crystallisation is to proceed under ordinary pressure, and the receiver to be thus used as an ordinary desiccator, it is only necessary to close the stopcock. If the pressure is

to be reduced, the stopcock is opened and the tube connected to the air-pump, water-pump, or, in case the laboratory is supplied with automatic vacuum, to the bench vacuum connection tap. As soon as the pressure has been reduced to the desired amount, the stopcock is closed and the receiver thus isolated. It is often convenient, if a large number of crops of crystals are to be prepared, to possess a battery of half a dozen such desiccators, as shown in Fig. 6, and to connect them to the vacuum producer through the intervention of a glass main tube directly connected with the latter, and having the corresponding number

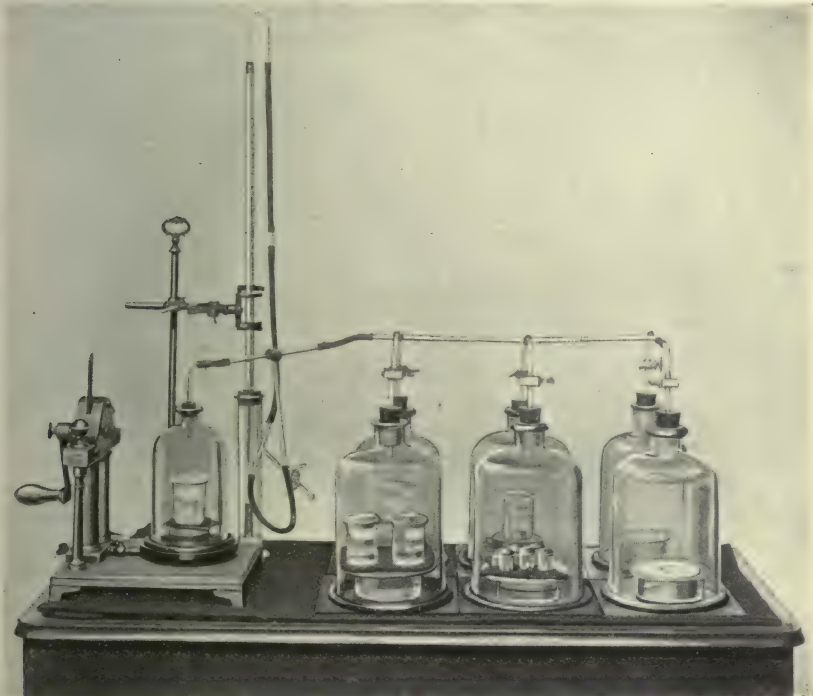


FIG. 6.—Apparatus for Crystallisation under Reduced Pressure.

of little side tubes blown on it, whereby to make the connections to the stopcock tubes of the receivers. All six can then be exhausted at once. If, however, the pressure is to be different in the different cases, which is rare, the receivers can just as readily be separately exhausted. It is an advantage that the main tube should be attached to a simple form of manometer, for indicating immediately the pressure in the receivers or any particular receiver before shutting off the taps. It is only necessary to use a long narrow glass tube for this purpose, carried vertically upwards at first on leaving the connection, then bent over and brought closely parallel to itself vertically downwards into a cup of mercury. But it is more convenient to have a partially caoutchouc (thick walled) connection,

as shown in Fig. 6, which can be broken for the insertion of an open T-piece with stopcock, for convenience in readmitting the air. The height of the manometer tube should obviously be somewhat over thirty inches, and a simple scale of millimetres or inches should be provided to indicate the height of the mercury in the tube above the level of that in the cup.

**Larger Crystals for Use in Optical Investigations.**—Before leaving the subject of the preparation of crystals suitable for the purpose of investigation, it may be remarked that crystals of somewhat larger size than those best suited for goniometrical work are an advantage in studying the optical properties, provided the internal structure is uniform throughout, as indicated by their perfect transparency. For these optical purposes it is necessary to prepare, by cutting or grinding, parallel-sided section-plates and 60°-prisms out of some of the crystals. The reduced pressure method just described may often be employed with success, but an even better method is to effect the crystallisation at the ordinary pressure, but in a large confined chamber containing as usual a dish of sulphuric acid, so as to permit evaporation to proceed with little restraint. A glass case 28 inches long, 18 inches wide, and 16 inches high, mounted on a cloth-covered wooden base with a fairly tightly fitting plinth, has served the author's purpose well. The dish of vitriol is set in the centre, and the crystallising beakers at regular intervals around. As fast as evaporation of the water of the solutions occurs, the vapour is absorbed by the sulphuric acid. Excellent crystals of many inorganic salts have been obtained by this method, of extraordinary perfection as regards development, planeness of the faces, and internal homogeneity; and of adequately large size not only for use in the optical investigation, but also to enable sufficiently large section-plates to be cut from them for use in demonstrations with the lantern projection polariscope.

A method of growing very large crystals from solution, for use in physical experiments (such as studying the electrical properties), has been described by R. W. Moore,<sup>1</sup> as applicable at any rate to crystals of Rochelle salt, sodium potassium tartrate<sup>2</sup> ( $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ). A saturated solution is made up at some convenient temperature, usually 35°-40° C., heated to a temperature 7°-8° higher, and filtered through paper on a Büchner funnel maintained at 4°-5° above the saturation temperature. Small "seed" crystals are then placed in a jar, the salt solution is poured in upon them, the jar is at once covered with a glass plate and placed in a large water-bath maintained with the aid of a sensitive thermostat at a temperature half a degree higher than the saturation-point. The temperature is then allowed to fall right away to saturation-point, and then subsequently at the rate of only one-tenth of a degree per day until the seed crystals have grown into larger perfectly clear and well-formed crystals. This stage frequently only occupies one day. After this the rate of fall can be increased to a fifth of a degree, and when the crystals have attained an inch in length the rate may be

<sup>1</sup> *Journ. Amer. Chem. Soc.*, 1919, **41**, 1060.

<sup>2</sup> This salt is known both as Seignette salt and Rochelle salt, Seignette, its discoverer in 1672, having been a chemist at Rochelle.



still further increased up to half a degree per day. This can go on in the case of Rochelle salt until the ordinary room temperature is reached, when the crystals, now of considerable size, should be removed, and dried with a soft cloth. The "seed" crystals referred to as being employed as nuclei to start the crystallisation are ordinary small crystals, about 5 mm. long and 2 mm. thick being a very suitable size.

**The Conditions for Crystallisation from Solution.**—In order that we may apply the preceding instructions with advantage, it is advisable that we should study in some detail the nature of the process of crystallisation, so far as it is yet understood. The elementary fact that every soluble substance dissolves in the solvent to a definite extent for every particular temperature, and that in general the extent or degree of solubility differs with the temperature, and is usually greater the higher the latter, has been assumed in the preceding sections. The interdependent relations of solubility and temperature are represented by the well-known "solubility curve," which is obtained by plotting a curve in the usual manner on squared paper, taking temperature for abscissæ and concentration (relative amount of the salt in solution as compared with the amount of the solvent present) for ordinates. Any point on the curve indicates by its co-ordinates the amount of the substance which the solvent can hold in solution at a specific temperature. For instance, Fig. 7 shows the solubility curve of ammonium selenate,  $(\text{NH}_4)_2\text{SeO}_4$ , constructed from a series of actual determinations by the author of the solubility of the salt at different temperatures. It is nearly a straight diagonal line, the dotted line being a truly straight one also drawn for comparison, and it indicates that at  $10^\circ \text{C}$ . 121 parts by weight of ammonium selenate dissolve in 100 parts of water, while 197 parts of the salt are dissolved by 100 parts of water at  $100^\circ$ , for intermediate temperatures the amount being nearly proportionately intermediate, as for instance at  $60^\circ$  when 165 parts dissolve in 100 of water.

Although it is a general rule that the higher the temperature the greater is the quantity of salt which can be held in solution, and that the difference in solubility for the neighbourhood of the ordinary temperature and for  $100^\circ$ , the boiling temperature of the common solvent water, is considerable, still there are many exceptions to the rule, and many cases where solubility increases up to a definite temperature and then diminishes again, particularly where the salt is one which crystallises with water of crystallisation. Also there is one notable case, that of common table salt, sodium chloride,  $\text{NaCl}$ , in which the solubility is almost the same at all temperatures of the solvent, water; thus 100 grammes of water at  $14^\circ$  dissolve 35.87 grammes of salt, whereas at the boiling temperature,  $100^\circ$ , only the slightly greater amount 39.61 grammes are dissolved. Hence the divergence in solubility of different salts or other soluble chemical compounds is very great, and each case has to be most carefully determined experimentally, and its curve constructed, if we wish to have trustworthy data regarding the solubility. For this reason the author always includes determinations of solubility in his crystallographic investigations of soluble salts.



But bearing these facts in mind, it is, broadly speaking, the general increase in solubility with rise of temperature which, as we have seen, gives rise to the regular deposition of the dissolved substance out of the solvent in the form of crystals, on the cooling of a solution which had been saturated at a temperature higher than the atmospheric, down to the latter. The amount of the solid substance thus deposited in crystals corresponds to the excess over and above the amount of the solid which the solvent can hold at the lower temperature of equilibrium with that of the atmosphere.

While this fact is roughly true, there are many interesting points of

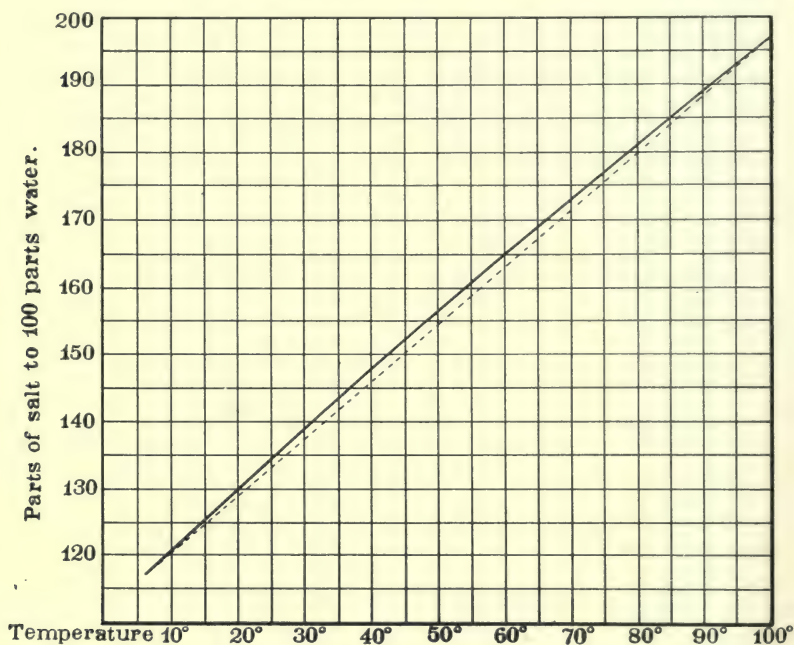


FIG. 7.—Solubility Curve of Ammonium Selenate.

slight variation which the crystallographer is bound to observe in the course of a lengthy experience and to take account of. For instance, it is frequently observed that when a solution has been brought to the condition in which, on cooling down to the atmospheric temperature, it ought to crystallise if it immediately obeyed the rule in accordance with its solubility curve, it declines to do so; and it may still refrain from crystallising, if the room be quite still, for some days. The solution is then obviously in a supersaturated condition. Eventually, however, under conditions which will presently be explained, crystallisation does occur, generally accompanied by the disengagement of heat, and proceeds very rapidly until the excess of the solid corresponding to the degree of supersaturation has been deposited in the crystalline form. Moreover, it

is an interesting fact that the crystallisation frequently goes too far, that is, further than just sufficient to bring about the theoretical equilibrium corresponding to the degree of solubility at the temperature of the atmosphere and solution. It is as if the molecules of the dissolved substance are carried down with such impetus by the crystallising forces, when once set in action to produce the regular solid, that the liquid is positively brought into a state of slight under-saturation. The result is that if crystals are left in the solution for any considerable time after they have formed (assuming no appreciable evaporation to occur so as to reduce the solvent and render the liquid again saturated), their edges will become rounded owing to this excess of crystalline matter redissolving again when the solution and crystals have time to establish full equilibrium. For true equilibrium is only attained when the solid phase (the crystals) and the liquid phase (the solution) have been allowed to remain for some time in contact. This rounding of the solid angles is also increased by the rise of temperature which accompanies rapid crystallisation, although the two causes are quite distinct, and the interesting phenomenon is particularly noticed in the cases of rapid crystallisations from strongly supersaturated solutions, and in those cases more especially when large rapidly formed individual crystals are the result. These are not conditions, however, which have been recommended in the foregoing pages as suitable for the growth of measurable crystals; for, as we have seen, solutions only slightly supersaturated are infinitely preferable for our purpose.

The phenomenon of over-crystallisation, and the subsequent rounding of the crystals produced if allowed to remain in the mother liquor, has been mentioned here because it is one that has not hitherto attracted the attention which it merits, and one with which the practical crystallographer has to reckon, and most of all to avoid, by eliminating all conditions conducive to rapid crystallisation, which is always, moreover, provocative of distortion.

**Supersolubility.**—The phenomenon of “supersaturation,” the converse of “over-crystallisation,” is not confined to a few substances, such as the well-known instance of sulphate of soda, but is a much more general one than was formerly thought to be the case. The main conditions in general are that the cooling solution shall remain tranquil, protected from all disturbance (although this is not essential in the case of sulphate of soda, which does not spontaneously crystallise at temperatures above  $-8^{\circ}$ ), and particularly, in all cases, including that of sulphate of soda, that it must be protected from the intrusion of dust particles from the air.

The common lecture experiment, with a strongly supersaturated solution of sodium sulphate, illustrating supersaturation, may just be recalled in passing. As much of the crystallised salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , as corresponds to nearly the correct amount for saturation at the temperature of  $32.5^{\circ}$ , at which temperature sodium sulphate exhibits its maximum degree of solubility, is dissolved in water in a large flask. One hundred parts by weight of water dissolve as much of the crystallised salt  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  as corresponds to 50 parts of  $\text{Na}_2\text{SO}_4$  at  $32.5^{\circ}$  and less than this amount at any other temperature, so that the strongest supersaturated solution can be made by dissolving as much of the salt as possible at  $32.5^{\circ}$ . The reason for this maximum

in the curve is that above  $32.5^\circ$  the decahydrate decomposes, losing its water and then dissolving as the anhydrous salt  $\text{Na}_2\text{SO}_4$ , which is abnormal in exhibiting decreasing solubility as the temperature rises. These interesting facts are graphically expressed by the curves given in Fig. 8, which are combined in one diagram from a paper by Hartley, Jones, and Hutchinson (*Journ. Chem. Soc.*, 1908, vol. 93, p. 828). The neck of the flask should, immediately after completion of the solution of the powdered crystals, be plugged with cotton wool, to filter out any dust particles which might otherwise intrude themselves, and be set aside to cool; it may then be preserved for an indefinite time without crystallising. But if the plug be removed and a small crystal of the salt be dropped in, crystallisation instantly occurs, and in fact the whole contents of the flask become a semi-solid white mass of crystals. A considerable rise of temperature accompanies the act of crystallisation, for the energy

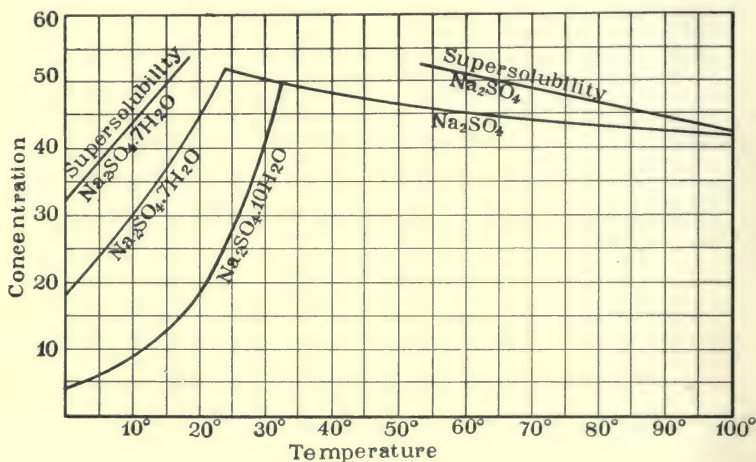


FIG. 8.—Curves of Solubility of Sodium Sulphate.

expended when a solid is converted into the liquid condition by the action of a solvent is given out again in the form of heat on the liquid resuming its solid condition. The supersaturated solution may also be caused to crystallise spontaneously by cooling it down to  $-8^\circ\text{C}$ , even when the plug of cotton wool is maintained in the neck. The experiment is still more effective if the warm concentrated solution of sodium sulphate be placed in a tube closed at one end and drawn out near the other, in such a manner that the solution may be boiled; while steam is issuing from the drawn-out portion the latter can be fused and sealed off at the blowpipe. If the sealed tube be then left to cool to the ordinary temperature, or even to  $0^\circ$ , no crystallisation occurs, although crystallisation would occur if it were further cooled in a freezing mixture to  $-8^\circ$ . But if the end of the tube be broken off and air admitted, crystallisation almost at once begins at the small surface at the top of the liquid column, where the air impinges, and rapidly spreads down the tube till all is apparently a solid mass of white interlacing crystals, the tube feeling distinctly warm to the hand. If the tube and solution are cooled in powdered ice to  $0^\circ$  before the point is broken off, the temperature at once rises, on crystallisation, to  $18^\circ$ .

Löwel<sup>1</sup> was the first to investigate systematically the reasons for the crystallisation or non-crystallisation of such supersaturated solutions of

<sup>1</sup> *Ann. chim. phys.*, 1850 (3), 29, 62.



Glauber's salt (as the decahydrated sodium sulphate is commonly called) ; and he discovered the interesting fact that the air in contact with the solution had something to do with it, and eventually attributed it to "catalytic" action of some constituent of the air. He found that if the air were washed by passage through water, crystallisation was delayed, but also that the converse process, passing the air through drying agents such as sulphuric acid or caustic alkalies, had the same effect, so that it was not a question of moisture but of something removed mechanically by the wash-liquid. Moreover, even passage of the air through a series of empty flasks delayed the crystallisation of the sodium sulphate solutions left in contact with the air so treated, and, best of all, filtration of the contact-air through cotton wool was most effective in arresting crystallisation.

Shortly afterwards, at one and the same sitting of the French Academy, a remarkable coincidence occurred, of a character which has not been rare in the history of science, for two different experimenters, Violette<sup>1</sup> and Gernez,<sup>2</sup> communicated papers in which practically identical conclusions were arrived at, fully explaining the interesting phenomenon in question. The facts presented were briefly these :

(1) The crystallisation of supersaturated solutions of Glauber's salt is brought about by the introduction of a solid substance from the air. For the crystallisation occurs the more rapidly the greater the extent of the surface of the solution which is exposed to the air. Thus it occurs more rapidly in an open dish than in a flask, and in the latter the crystallisation is the slower the narrower the neck. Air from the country is more sterile than the air of towns, and when performing the experiment in the country crystallisation occurred more slowly if the experimenter changed his clothes for others which had not travelled with him from the town.

(2) The substance thus causing crystallisation is soluble in water, and it loses its property of inducing crystallisation when it is heated.

(3) The air which causes crystallisation contains sodium sulphate. The air of towns notoriously contains traces of the salt, owing to the combustion of coal in domestic and industrial fires, which send small but easily detectable quantities of sulphurous acid into the atmosphere, where it becomes oxidised to sulphuric acid, which then (or possibly the sulphurous acid before oxidation) combines with the traces of soda which are well known to be universally present in the air, to form sodium sulphate (or sulphite which becomes oxidised to sulphate).

The conclusion is obvious, namely, that the substance in the air causing the crystallisation of supersaturated solutions of sodium sulphate is **that substance itself**, disseminated in the air in excessively minute crystals.

Gernez afterwards<sup>3</sup> extended his observations to other substances, and discriminated clearly between those supersaturated solutions which do not spontaneously crystallise, but require the introduction of a germ-crystal of the same substance, and those which crystallise on shaking,

<sup>1</sup> *Comptes rendus*, 1865, 60, 831.

<sup>2</sup> *Ibid.*, 1865, 60, 833.

<sup>3</sup> *Ibid.*, 1865, 60, 1027.



on rubbing the sides of the vessel with a glass rod, or on employing other modes of disturbance which bring about spontaneous crystallisation, the temperature at which the latter occurs (except in the case of sodium sulphate, where it is  $-8^{\circ}$ ) being generally readily observable. But Gernez does not appear to have recognised that the same substance shows both kinds of supersaturated solutions, and considered that the class to which a substance belonged was a property of the substance.

A further step was next made by Lecocq de Boisbaudran,<sup>1</sup> who showed that not only were crystal-germs of the substance itself able to provoke the crystallisation of supersaturated solutions, but that also germs of such substances as were isomorphous with the substance were able to do so. Gernez<sup>2</sup> about the same time made the particularly interesting discovery, that not only the crystal system required to be the same in order to call forth crystallisation, but also, in the case of crystals belonging to other than the holohedral class of any system, that is, crystals showing less than the full symmetry of the system, the particular variety must be the same. For instance, a solution of sodium ammonium racemate (racemic acid being a molecular compound of ordinary dextro-tartaric acid and of lævo-tartaric acid) which on crystallisation had previously been found by Pasteur to yield an equal mixture of right-handed and left-handed crystals (the two varieties of the rhombic bisphenoidal Class 6, Chapter XIV.) of sodium ammonium dextro- and lævo-tartrates, on contact with a crystal of the right-handed variety of sodium ammonium tartrate only deposited right-handed crystals of the dextro-salt, whilst a left-handed crystal of complementary enantiomorphous symmetry produced a crop of left-handed crystals of the lævo-tartrate; the right-handed salt has no power of compelling the crystallisation of the left-handed variety, and *vice versa*.

A still further interesting step was then made by J. M. Thomson,<sup>3</sup> who showed that strict isomorphism was essential in the crystal-germ, that for instance the crystallisation of an alum solution, although the simple forms of the cubic system (the cube, octahedron, and rhombic dodecahedron) in which the alums crystallise are alike for all substances, was not provoked by cubic crystals of common salt or by octahedral or rhombic dodecahedral crystals of magnetic oxide of iron. It will be shown in Chapter XXX. that this means that not only must the form but also the internal structure of the crystalline substance be the same, an exceedingly important point. It will subsequently be shown that the index to such structural similarity is practical identity of the volumes of the unit cells of the structural space-lattice (both the molecular volumes, which are relative measures, and the absolute volumes); and also of the distances of separation of the centres of gravity of adjacent structural units, the chemical molecules or small groups of molecules forming the structural units, along the crystallographic axial directions, which distances are expressed relatively by the constants termed "molecular distance ratios," or "topic axial ratios" (the linear dimensions of the cells), a full account of which will be given in Chapter XXXI.

<sup>1</sup> *Ann. chim. phys.*, 1866 (4), 9, 173.

<sup>2</sup> *Comptes rendus*, 1866, 63, 843.

<sup>3</sup> *Zeitschr. für Kryst.*, 1881, 6, 94.

Other chemists and physicists have from time to time added further data concerning supersaturated solutions, notably de Coppet, Lefebvre, Roozeboom, and Ostwald.<sup>1</sup>

All agree that among supersaturated solutions there are those which, when crystal-germs are excluded, may be preserved under certain conditions apparently for an unlimited length of time without spontaneously depositing crystals (forming the solid phase, as it is termed by Ostwald, in conformity with the nomenclature introduced by the acceptance by physical chemists of the "phase rule" of Willard Gibbs). Such solutions were called by Ostwald "metastable." Others there are which after a short time, assuming germ-crystals also excluded, spontaneously develop the solid phase. These Ostwald termed "labile."

Metastable solutions always exhibit a lower concentration compared with the labile solutions of the same substance. By increasing the concentration the metastable solution passes consequently into the labile condition, and the particular concentration for which the change occurs was termed by Ostwald the "metastable limit." The metastable limit depends chiefly on the nature of the substance, the temperature, and the pressure. It is also influenced by certain other conditions to be defined later.

The state of supersaturation can be removed, not only by the agency of solid germs (excessively minute crystals) of the dissolved substance itself, but also by the action of solid germ-crystals of a substance isomorphous with it, and possessing close similarity of molecular volume and of the molecular distance (topic axial) ratios to be described in Chapter XXXI. Indeed some substances may effect the same object which are not strictly isomorphous, but which form mixed crystals with the substance dissolved, the formation of mixed crystals having been shown to be due to the possession of almost identical molecular distance (topic axial) ratios.

The quantity of the solid substance which, in the form of a crystal-germ, can exert this influence, is very minute, but not undeterminably so, direct experiments having indicated an order of from  $10^{-9}$  to  $10^{-12}$  of a gramme of the solid substance for the weight of the germ-crystal. The latest determinations, indeed, by D. McIntosh,<sup>2</sup> have given results with sodium sulphate even smaller than this, varying from  $10^{-12}$  to  $10^{-18}$  gramme.

The means of defining the metastable limit and of constructing the supersolubility curve graphically representing it have now been discovered by Sir Henry Miers,<sup>3</sup> who has also added considerably to our further knowledge of the behaviour respectively of both metastable and labile supersaturated solutions. When, instead of allowing the cooling supersaturated solution to remain at rest, it is continuously stirred in an open vessel, only a slight shower of crystals appears when the temperature of saturation, indicated by the ordinary solubility curve and corresponding to the amount of salt present, is attained, and the liquid then continues to cool without depositing the main bulk of the excess—which one might

<sup>1</sup> *Lehrbuch der allg. Chemie*, vol. ii. part ii. p. 780.

<sup>2</sup> *Trans. Roy. Soc. Canada*, 1919, 13, iii. 265.

<sup>3</sup> *Phil. Trans.*, 1903, A, 202, 459; *Journ. Chem. Soc.*, 1906, 89, 413; *Proc. Roy. Soc.*, 1907, A, 79, 322.



expect would crystallise out if the ordinary solubility curve represented the whole truth—until a temperature about  $10^{\circ}$  lower than the saturation temperature is reached, when a second and much more copious shower of crystals falls, corresponding to arrival at the metastable limit. When, however, a closed vessel is used, a sealed tube for instance, the first shower never falls at all, nothing whatever occurring until the temperature  $10^{\circ}$  lower than the saturation temperature is reached, when the whole excess corresponding to the two showers added together is suddenly and rapidly precipitated in the crystalline form. The tube may be shaken for any length of time above this temperature without any deposition of crystals occurring. This latter observation is a confirmation of the experiments of the previous observers already referred to, but the novelty of Miers' work consists in the isolation of two distinct showers, corresponding to the ordinary and the supersolubility curves, by the continuous-stirring method in open vessels. The deposition of the first slight shower is due to crystallisation being started by inoculation of the solution with crystal-germs of the same or an isomorphous or structurally similar substance introduced from the air, while the second shower at the lower temperature is due to the spontaneous crystallisation of the excess of solid. The first shower thus corresponds to the ordinary solubility curve, which may be said to be the curve of crystallisation by inoculation, and the second shower to the supersolubility curve of spontaneous crystallisation, the "metastable limit" of Ostwald. The interval between the two curves represents the "metastable condition" of the supersaturated solution, and the condition for spontaneous crystallisation corresponding to the area of the curve-diagram beyond the supersolubility curve corresponds to Ostwald's "labile condition." Fig. 9 on page 24 will assist in rendering this clear.

Miers has carried the subject an important stage further by his discovery of an admirable method of experimentally tracing the supersolubility curve. A glass prism of known refractive index is mounted on the crystal-holder of an inverted goniometer, and immersed in the solution, which is contained in a glass trough the front part of which facing the observing telescope is formed by a parallel-faced truly plane plate of glass, and the refractive index of the solution is determined by the method of total reflection within the prism. The mode of procedure, illustrated by a figure showing the actual instrument (Fig. 331), will be fully described in Chapter XLVII. on refractive index determinations. Such determinations of refractive index were found to be possible during the whole course of the cooling and stirring of the solution, and to afford an exact means of determining when the labile shower of crystals commences to fall. For the instant crystals begin to be deposited the refractive index shows a corresponding marked diminution, and a thermometer immersed in the solution indicates the temperature. The change in refractive index is very slight at the temperature corresponding to the ordinary solubility curve, but much more considerable and very sudden at the temperature of the supersolubility curve, the two changes corresponding to the slight and the copious nature of the two respective crops of crystals. As the ordinary solubility curve is determined accurately by the usual well-



known methods, based upon the estimation of the actual amount of dissolved substance contained in a given amount of the solution, which is always decanted for the purpose from above crystals with which it has been lying in equilibrium-contact for some time previously, attention need only be concentrated on the determination of the temperature and concentration corresponding to the deposition of the copious crop at the metastable limit, and the estimation is a very accurate one at this stage, owing to the suddenness of the change and copiousness of the crop. By making a large number of such observations with solutions of various degrees of concentration, observing the change with each as it fell from a temperature of about  $50^{\circ}$  until the crystal cloud appeared, and then combining the results, the supersolubility curve was accurately traced, for it followed the maxima of all the individual curves, and it was found to lie generally more or less parallel to the ordinary solubility curve at a distance indicating an almost constant difference of about  $10^{\circ}$ .

The explanation is as follows. As the refractive index of a soluble solid substance is greater than that of pure water, the refractive index of the solution is higher than that of water, and is the higher the greater the amount of salt present, that is, it rises with the concentration. As, moreover, the refractive index is generally reduced by raising the temperature of the refracting solid or liquid, it follows that the refractive index of a solution cooling slowly for  $50^{\circ}$  without evaporation (a layer of oil being placed on the top to prevent this) shows a rising refractive index until the labile cloud of crystals appears (the slight metastable cloud scarcely affecting it), when the sudden removal of solid causes a correspondingly sudden fall in the refractive index, the effect being greater than merely just enough to arrest the growth of the index. Hence, when the concentration is accurately known, it is only a matter of ascertaining the temperature at the exact moment when the maximum refractive index is observed. But the slight metastable crystallisation, corresponding to the ordinary solubility curve, alters the concentration from that originally started with, and somewhat complicates matters. The actual maximum refractive index at the instant the labile cloud forms is itself, however, an infallible indication of the true strength of the solution at the moment, provided, as was actually done, a preliminary series of determinations of the refractive indices of clear solutions of known strengths at different temperatures had been made. Hence the method is really very simple and complete in itself.

The advantage of this over any method based on mere observation of the formation of the cloud of crystals lies in its precision, for the liquid is already usually turbid from the formation of the first slight shower and an amount of slow growth of crystals which follows it, so that it is not possible to see clearly when the labile cloud first begins to form. The idea of making the solution record its own strength at the critical moment by its refractive index, and the moment afterwards to indicate that same critical point by its sudden jump in refraction, is an ingenious one.

In Fig. 9 are given a typical pair of solubility and supersolubility curves. The lower one marked S is the ordinary solubility curve, and the

upper one lettered SS is the supersolubility curve. The dotted curve ABCD shows the normal course of the crystallisation of a solution made by adding the salt to hot water, and which is stirred while being allowed to cool. The solution cools from A to B without anything being observed. But at B crystals make their appearance, forming from germ-crystals introduced from the air. From B to C the liquid is still cooling and crystals are growing slowly, but at C the labile condition is reached at contact with the supersolubility curve, and a cloud of crystals is deposited, the concentration falling rapidly to D on the solubility curve, in most cases with a rise of temperature. It will be noted that crystallisation

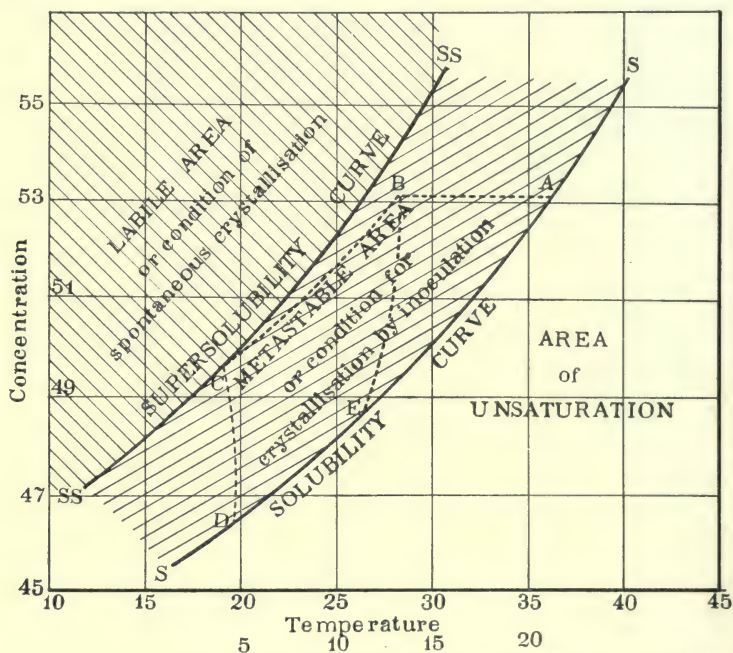


FIG. 9.—Diagram explanatory of Labile and Metastable Conditions of Supersaturated Solutions.

does not necessarily begin immediately on entering, at the solubility curve, but usually well inside the metastable region between the two curves. For it will probably happen that a germ-crystal does not enter until after the condition corresponding to first contact with the solubility curve has been attained. But the spontaneous crystallisation of the heavy cloud occurs quite sharply at C, the point of contact with the supersolubility curve, when the solution is agitated by stirring. If the solution were allowed to cool at perfect rest, however, crystallisation might not occur until the labile condition had been well entered, at some point beyond the supersolubility curve, if it so happened that a germ-crystal did not fall into the solution until this degree of concentration had been attained.



In the important case of a not too strong solution crystallising at rest, from the metastable condition,—the case which the author has recommended in the previous pages as the most suitable for growing good crystals for the purposes of measurement,—the crystals are first started by inoculation from the air, say at B, while the solution is only very slowly cooling from A to B. The concentration then diminishes by withdrawal of material from the solution, and the change of temperature being so slow, the labile condition is never reached, the course of the crystallisation being indicated by the dotted curve BE, for which the temperature abscissæ given below the word temperature are more suitable. Thus no cloud of crystals is produced, but only the further steady growth of the crystals first started, the very conditions desired.

In the previous Fig. 8 (page 18) the supersolubility curves are also drawn of anhydrous sodium sulphate,  $\text{Na}_2\text{SO}_4$ , and the heptahydrated salt  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , as given by Hartley, Jones, and Hutchinson in the memoir already alluded to. The decahydrated salt does not appear to possess a definite limit of supersolubility. The crystals obtained by these authors by spontaneous crystallisation, as distinct from those induced in the lecture experiment by the access of germ-crystals, consisted of the heptahydrated salt in the great majority of cases, the decahydrated salt being of comparatively rare and irregular occurrence, except when the cooling occurred very swiftly to  $-10^\circ$ .

It has thus been abundantly proved to be a highly important fact that a crystal can only grow in a more or less (labile or metastable) supersaturated solution, or, in the case of a molten metal or other fused substance, from liquid which is to a certain extent undercooled. In the immediate neighbourhood of the crystal there is a zone of liquid which has become no longer supersaturated, owing to removal of the solid substance by deposition on the crystal, in continuation of the growth of the latter. Further growth is arrested until more supersaturated solution is supplied to the zone by diffusion or convection. The concentration currents thus set up are strongest at the sharp angles of the crystals; hence, growth is there accelerated, giving rise in labile solutions to excess of growth in axial directions, and production of skeletal, acicular, arborescent, or fern-like crystals. It is only when the supersaturation has again fallen to the metastable condition that the growth is sufficiently slow for it to occur evenly all over the crystal, when a perfect polyhedron is produced.

As the result of surface tension experiments P. Curie<sup>1</sup> showed that a crystal tends to assume that shape in which the sum of the surface energies is a minimum. As the faces of different "forms" have different capillary constants, crystals do not become spheres, as drops of liquid do under the influence of surface tension when free from the action of external forces, but strive to attain a condition in which the total surface has the minimum area compatible with the crystal structure. Hence, when crystals of various sizes are placed in contact with a saturated solution of the same substance, the smaller crystals tend to disappear, the matter

<sup>1</sup> *Bull. de la Soc. Min.*, 1880, 8, 145.



of which they are composed passing into solution, and being redeposited on the larger crystals. Equilibrium is only reached, according to Curie, when the whole of the material has become collected into one large crystal.

A beautiful experimental demonstration of crystallisation from the metastable and labile conditions of solution respectively is afforded by potassium bichromate,  $K_2Cr_2O_7$ . When crystallised from a metastable solution under conditions of quietude, this salt is slowly deposited in bright orange coloured and excellently formed individual crystals, often of considerable size, belonging to the triclinic system of symmetry; they are bounded by good pinakoidal (pairs of parallel) faces intersecting in sharp edges. But when the crystallisation occurs from a labile solution, being much more rapid it takes the form of feathery or arborescent branching skeletal growths, there being inadequate time for the formation of well-developed crystals. Fig. 10, Plate I., is a photographic reproduction of good crystals of the salt, grown from a drop of metastable solution on a microscope slip, just as they were seen through the microscope in the slow act of formation, employing a  $1\frac{1}{2}$  inch objective. The crystallisation had been started by germ-crystals of the salt falling in from the air, after which the drop, placed within a ring of hardened gold-size on the slide, had been covered with a thin cover-glass, under which the crystallisation had proceeded with sufficient slowness to enable a successful photograph to be taken, when the camera was attached above the vertically arranged microscope.

Fig. 11 is the reproduction of another photograph, taken when a hot and more concentrated solution of potassium bichromate was used, at the moment when a rapid labile crystallisation was just completing itself, the cooling through the metastable condition having been too rapid for a germ to fall in and start the metastable crystallisation before the labile condition was reached. The rapidity of growth had just begun to be arrested when the exposure was made. Indeed, the branches are seen to be terminated frequently by small well-formed crystals, the rapid growth having been succeeded by a final slow crystallisation where the solution had discharged its labile excess and attained once more the metastable condition. The experiment succeeds admirably as a screen experiment with the lantern microscope. Not only do the arborescent crystallisations shoot out from the margin of the field, but on exploring the whole contents of the gold-size ring-cell the feathery growths are seen to appear suddenly radiating from a number of different centres, traversing the field rapidly, and finally becoming arrested and developing the little well-formed crystals like fruit at the ends of the branches. The bright orange colour of the crystals renders them all the more visible, and the whole appearance on the screen is one of an unusually beautiful character.

Another excellent example of a labile crystallisation is afforded by ammonium chloride, crystallised in the same manner in a shallow cell on a microscope slip. Fig. 12 is a reproduction of a photograph of such a field of rapidly crystallised ammonium chloride. This case is also very suitable for screen demonstration. The tracery of skeletal growths



FIG. 10.—Potassium Bichromate slowly crystallised from a Metastable Supersaturated Solution.

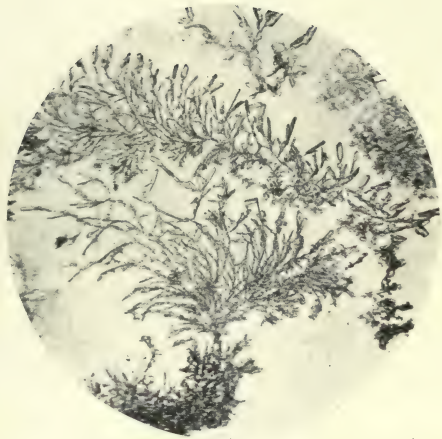


FIG. 11.—Potassium Bichromate rapidly crystallised from a Labile Supersaturated Solution.

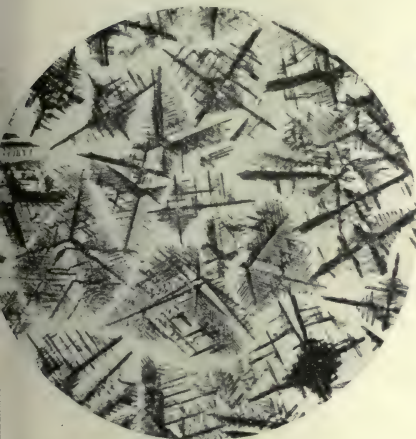


FIG. 12.—Ammonium Chloride crystallised from a Labile Supersaturated Solution.

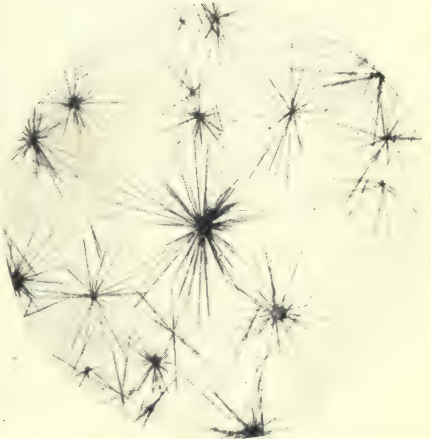


FIG. 13.—Needle Clusters of Calcium Sulphate produced by Precipitation.

REPRODUCTIONS OF PHOTOMICROGRAPHS ILLUSTRATING CRYSTALLISATION FROM THE METASTABLE AND LABILE CONDITIONS OF SUPERSATURATION.





represents an attempt at the production of octahedral crystals, the ramifications following the axial directions of the cubic system. On the other hand, if the crystallisation be retarded, as can be effected by the addition of a little urea to the solution, the salt crystallises in well-formed cubes.

Needle-shaped crystals are also characteristic of growth from a labile solution, because the growing crystal is surrounded by a sheath of protective metastable liquid, except at the one point of growth, the point of the needle, where it is in contact with the labile solution. An interesting case is illustrated in Fig. 13, that of calcium sulphate, gypsum, selenite,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . In this case the crystals were produced by the addition of a drop of dilute sulphuric acid to a weak solution of calcium

chloride, on a microscope slip ringed as before with gold-size. Owing to the slight solubility of calcium sulphate the labile condition is very rapidly reached, and these needle clusters are produced like stars, appearing all over the field. A one-inch objective was employed in taking this photomicrograph. The ordinary monoclinic crystals of gypsum are illustrated in Figs. 400 and 401 in Chapter XXVIII. While yet so different in appearance to selenite crystals, these needle clusters radiating from centres are yet composed of the same monoclinic prism, which, however, is relatively enormously developed compared with the end forms, thus taking up an acicular character.

Some crystalline precipitates formed not too rapidly also yield forms intermediate between perfect crystals and amorphous grains. Thus the yellow precipitate of potassium cobaltinitrite,  $\text{K}_3\text{Co}(\text{NO}_2)_6$ , formed by adding a solution of potassium nitrite to one of a soluble cobalt salt, takes the form of the star-shaped crystallites illustrated in Fig. 14.

Acicular crystallisation is sometimes observed in the case of metals solidifying from the molten state. A beautiful example is shown in Fig. 15, a crystallisation of metallic iron described by Grignon, so long ago as 1775, in the *Mémoires de Physique*, Paris. It was found in a cavity in a large mass of grey pig-iron, which had cooled slowly beneath a protecting layer of hot slag, and is typical of the large crystallites of iron, formed by growth along the octahedral axes.

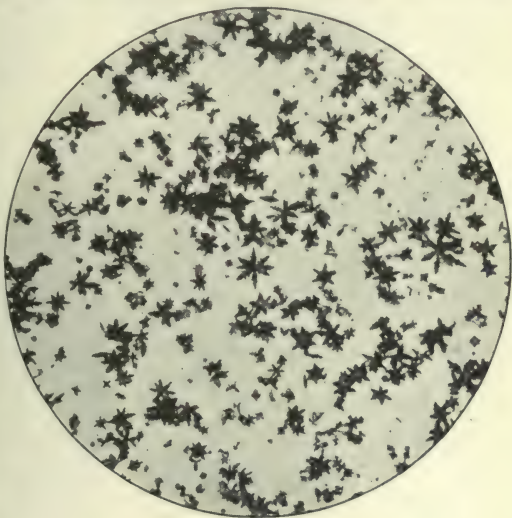


FIG. 14.—Star Crystallites of Potassium Cobaltinitrite.

It is not a far step from the acicular, arborescent, or feathery forms of labile crystallisation, of which examples have been given, to the dendritic forms of crystallisation, of which two beautiful examples afforded by frost patterns on glass windows are given in Fig. 440, Chapter XXIX., and of which also another instance is illustrated in Fig. 16, that of a dendritic deposit of the mineral pyrolusite, native manganese dioxide  $MnO_2$ , on sandstone. These crystallisations may be due either to skeletal deposition due to smallness of the quantity of

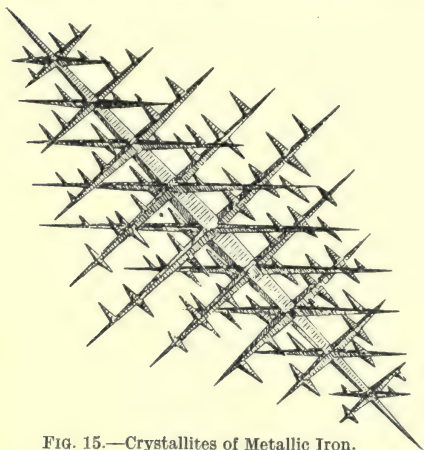


FIG. 15.—Crystallites of Metallic Iron.

available material, compared with the large extent of space over which it is spread, or to repeated twinning, or most probably to both causes.

The beautiful forms often exhibited in the earliest stages of or attempts at crystallisation should also be mentioned. The crystallites produced during the devitrification (slow crystallisation) of glass, or slag, or the natural glass obsidian (the glass produced by the vitreous solidification of certain lavas or deep-seated volcanic magmas) are excellent examples, and undoubtedly the most beautiful case is that of the pitchstone of the island of Arran, the arborescent and fern-like microliths of which are portrayed in Fig. 17. They are primitive attempts at the formation of crystals of hornblende.

These experiments and types of crystallisation have been described at some length because of their importance to the crystallographer, in teaching him the exact conditions under which crystallisation can and does occur. Usually, the conditions recommended in the previous section of this chapter will



FIG. 16.—Dendritic Pyrolusite on Sandstone.



correspond to the crystallisation of solutions only slightly supersaturated, most probably in the metastable state, the conditions being those of the region between the solubility and supersolubility curves. The solutions will be at as perfect rest as is attainable, but will be open to the air, thus permitting access of crystal-germs and also slow evaporation; hence crystallisation will probably be started by a crystal-germ of the substance itself, or of a substance isomorphous or isostructural with it, and it will proceed slowly and steadily, and as there is no agitation there will be no rapid acceleration of crystallisation if or when the labile state is attained, but a steady further accretion of crystalline material on the lines slowly and deliberately (and therefore perfectly orderly without distortion) laid down during the previous stage of metastability, that is, as a further growth on the same crystals.

In all probability the evaporation and crystallisation will eventually nearly balance each other, the former just keeping very slightly in advance and maintaining the solution very slightly supersaturated, that is, in the condition of metastability. It will also be understood how important is the instruction which has been given, to remove crystals from the mother liquor (when it is desired to collect them for use) early in the morning, before the

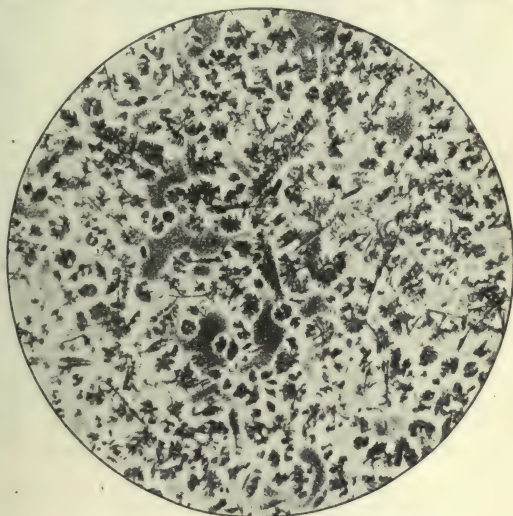


FIG. 17.—Crystallites of Arran Pitchstone.

rising temperature of the room and solution renders the latter less saturated and possibly slightly unsaturated, resulting in the crystals having their edges rounded, and their faces etched.

In concluding this chapter mention may be made of two remarkable series of experiments on crystal growth. The first are those of G. F. Becker and A. L. Day<sup>1</sup> on the linear force of growing crystals. It was established that a growing crystal has the power of raising a superimposed weight, provided it is alone in the solution. The explanation is that the effect of the load is to increase the solubility of the individual crystal placed under pressure, so that if other growing crystals, free from weights, are present they grow by preference rather than the individual under pressure. The "force of crystallisation" has thus been actually demonstrated as a mechanico-physical fact in these experiments.

The second are an interesting series of microscopic observations of

<sup>1</sup> *Journ. Geol.*, 1916, 24, 313.



the mode of development of crystals which have been carried out by R. Marcellin.<sup>1</sup> The substance first used was an alcoholic solution of paratoluidine. It was ascertained that the crystals grew by successive deposition of uniform layers arranged in steps, which first exhibited the grey of Newton and then the first-order colours. The minimum thickness observed was  $1.6 \mu\mu$ , which corresponds to only three molecular diameters. The heat rays were filtered off by alum solution during the observations and measurements. When the alum cell was removed the crystal invariably began to redissolve, and did so in uniform layers of the solid of definite thickness, the process of solution being thus of precisely the reverse nature to that of crystallisation. In a second series of experiments very fine laminæ of mica were used. They were obtained by the method of R. W. Wood, that is, by pressing a thin sheet of mica against fused selenium, and tearing the mica off again after cooling, when excessively fine films of the mica are left behind. In this manner laminæ as fine as only  $0.7 \mu\mu$  were obtained, which correspond to the thickness (diameter) of one molecule of mica only, on the assumption that the mica molecule is approximately spherical, an observation of the greatest interest and value, and to a thickness of only two or three molecules if the latter be flattened or tabular. Marcellin concluded from these observations that a solid crystalline structure may be perfect and complete when less than 20 molecules thick. It is much to be regretted that this careful and original investigator was killed in the War.

<sup>1</sup> *Ann. de physique*, 1918, [ix.], 10, 185 and 189.

## CHAPTER III

### THE GONIOMETER

It is astonishing how soon the apparent difficulties of crystallography disappear after a short acquaintance with the practical use of the goniometer. Owing to the more or less geometrical and mathematical foundation of the subject, and to the fact that this aspect of crystallography has usually been the one first brought to the notice of students, and is especially prominent in most of the text-books, many students who might otherwise have been attracted to an essentially fascinating and eminently practical study have been discouraged and repelled. If, instead, a few lessons on the practical use of the goniometer can be substituted, the fundamental principles underlying the symmetry of crystals, and the geometrical and numerical relationships of faces, unfold themselves so naturally and obviously that the learner is charmed as with a series of most interesting original discoveries. It will be the writer's object in this and the following chapters thus experimentally to lead the student onwards, introducing only sufficient theory at a time to render the practical steps already taken intelligible, and explaining it more fully when the actual phenomena have been personally observed.

Our prime duty is to understand thoroughly the reflecting goniometer, which has been vastly improved since its original invention by Wollaston in the year 1809. After a brief description of the contact goniometer for the measurement of large crystals, an account will first be given of the most accurate and at the same time handy form of horizontal-circle goniometer in use in the best laboratories to-day, and subsequently of a simpler and cheaper form of instrument, with a vertical circle, eminently suitable for student use.

**The Contact Goniometer** was invented by Carangeot of Paris in the year 1780, and was used by the earlier crystallographers Romé de l'Isle (for whom Carangeot also made a large number of crystal models, including more than 500 different forms) and the Abbé Haüy, previous to the invention of the reflecting goniometer by Wollaston. An illustration, about two-thirds the actual size, is given in Fig. 18 of an interesting duplicate of the original instrument, which came into the hands of the Duke of Buckingham, and was presented by him in the year 1824 to Prof. Buckland, and is now one of the treasures of the University Museum

at Oxford. The form of contact-goniometer in use to-day is practically the same, and that constructed by Messrs. Steeg and Reuter is represented in Fig. 19. It is still

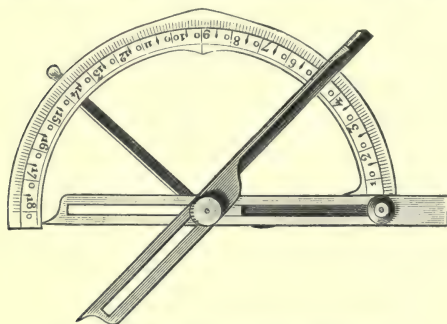


FIG. 18.—The Oxford Contact Goniometer.

of use in measuring the interfacial angles of large crystals, either because their surfaces are too dull to afford reflections on the reflecting goniometer, or because the crystals are too large to be mounted on the latter. It consists of a divided semicircular arc, to the centre of which a pair of slotted bars provided with straight edges (not bevelled) are pivoted, in such a manner

that they can be fixed at any angle by means of the pivot-screw. The crystal requires to be firmly supported while the two straight edges (really edge-strips, truly at right angles to the bar faces) are laid closely in contact with the two faces in question, the angle between which is to be measured. A sheet of white cardboard is placed well behind so as to afford a brilliantly white background, and the observer then looks along the direction of the edge between the two faces, and, while maintaining the plane of the instrument perpendicular to this edge, carefully adjusts the straight edges so that absolutely no trace of the white background is seen between them and the faces against which they are laid. The milled-headed nut of the pivot-screw is then tightened. One of the bars is set so that its straight edges are parallel to the diameter corresponding to the zero division of the semicircular arc. The central line of the

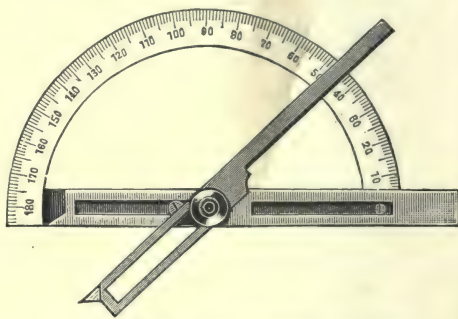


FIG. 19.—The Ordinary Contact Goniometer.

bar passing through the centre of the pivot is then over this zero mark. Two slots are cut in this bar, on both the right and left side of the pivot, as shown in the figure, and two pins within the slots permit only of the bar sliding along this line. The other inclined bar is cut away altogether on the right down to a bevelled edge, which forms the central line of the bar and thus indicates the correct angle between the straight edges on the arc. The measuring edge of the bar to be employed as straight edge is in each case indicated by the bar being made to terminate at a point lying in the edge in question. This particular edge of each bar has been made an absolutely straight line, as accurately as experimental skill can achieve it. The point is also useful when the instrument is



used with mineral crystals occupying a cavity in a matrix; the slots on the left also enable the bars to be shortened to any extent to facilitate the use of the instrument even when the cavity is quite shallow.

In the case of the instrument illustrated in Fig. 18, provision is made to move the left half of the semicircle out of the way, the arc being hinged at the  $90^\circ$  graduation, so that the left quadrant may be bent freely backwards. When in position it is fixed by the additional radial arm shown passing behind the  $140^\circ$  graduation, where it is secured to the back of the arc by a milled-headed screw; the other end is fixed by a nut to the pivot at the back end of the latter. The little instrument is beautifully constructed, largely of silver, and bears the name "Vutois Rochette à Paris." The outside diameter of the semicircle is 8 cm.

**The Reflecting Goniometer.**—The principle of this all-important instrument will be fully discussed with the aid of an explanatory diagram (Fig. 33) at the opening of the next chapter, in connection with the mode of use of the apparatus. It will suffice to say here, before passing to the description of the instrument itself, that its purpose is to measure the angle between any two faces on a crystal, by obtaining a reflection of the parallel light from a collimator (a tube with a lens at one end and an illuminated slit at its focus at the other end) from each of the two faces in succession, and receiving the reflected rays in a telescope, where an image of the slit, which latter is known as the "signal" or "signal-slit," is produced, and can be adjusted to the intersection of the cross-wires as reference spot. The angle through which the crystal requires to be rotated, in order thus to bring the two images one after the other to the reference spot, is measured on a divided circle, and is **the angle between the normals to the two faces**, the supplement of the real internal dihedral angle between the faces.

A telescope and collimator are not indispensable, a slit in a distant otherwise darkened window serving admirably as a signal, and a mirror carried by the goniometer and in which the light from the window slit is also reflected, affording an image of the slit which serves equally well as reference line to which the images reflected from the crystal faces can be allocated. But the most accurate goniometers are always supplied with collimator and telescope, like a spectrometer or spectroscope, the crystal replacing the prism. The best of these reflecting goniometers will be described first.

**The Fuess Horizontal-Circle Goniometer.**—One of the best forms of reflecting goniometer, with which many original investigations have been carried out, including those of the author, is that constructed by the firm of R. Fuess of Berlin, No. 2 model, and due to the recommendations of such well-known crystallographers as von Lang, Websky, von Groth, Liebisch, and others. It possesses a circle which reads with the aid of a vernier accurately to half-minutes. Its construction will be rendered clear by Figs. 20 and 21, the former representing the general appearance of the instrument, and the latter a vertical section on the scale of one quarter the actual size. It consists of three essential parts, (1) the rotating horizontal divided circle for the measurement of the angles,

(2) a telescope and collimator, the latter provided with the signal-slit, for the observation of the reflections of this signal from the crystal faces; and (3) a delicate but easily and rapidly manipulated apparatus for adjusting the crystal.

The whole is carried by a stout circular table of brass, *a*, supported by three feet provided with levelling screws, and having a hollow cone bored in its centre, where it is thickened. Within this boring rests, and is rotatable, the conical axis *b* which carries a circular plate *c*, provided at two diametrically opposite positions on inlaid

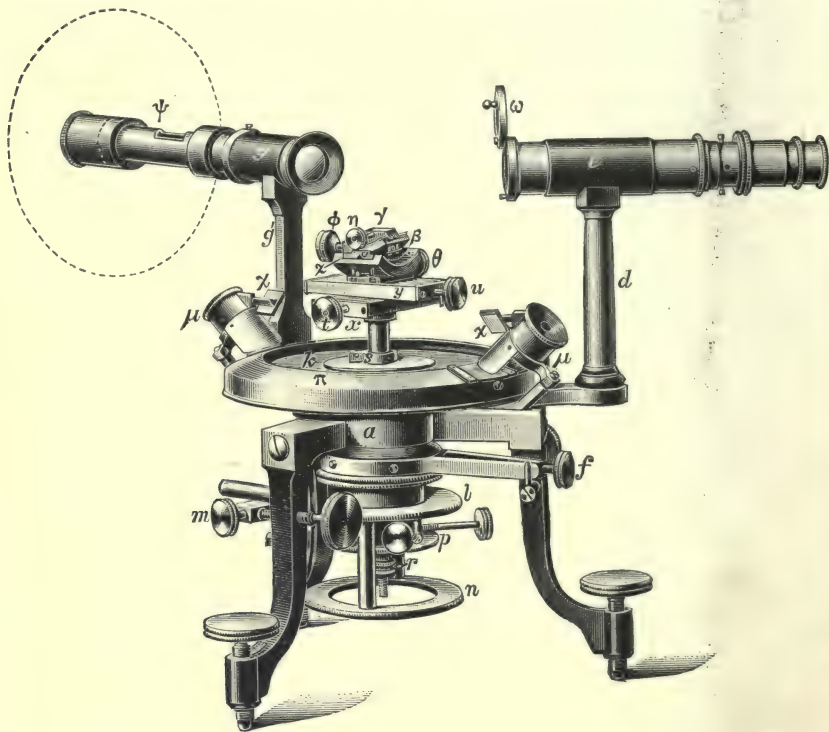


FIG. 20.—No. 2a Fuess Reflecting Goniometer.

silver arcs with vernier divisions, each of  $30''$ . To this vernier-circle there is rigidly attached, below, a horizontal arm, which carries at its outer end a vertical column *d* on which is supported the observing telescope *e*. Hence the latter moves with the vernier-circle, and both may be fixed at any position by the clamping screw *f*, which presses a ring against the lower flange of the rotating cone *b*. The collimator *g* is carried by a column *g'*, which is definitely fixed to the table *a*, so that when the clamping screw *f* is tightened the collimator and telescope are fixed relatively to each other, and this may be achieved at the angular position with respect to each other which is found most convenient for the observation of the reflections from crystal faces, which is usually somewhat over  $90^\circ$ .

In the hollow rotatable axis *b* a second similar one *h* is capable of rotation, which carries at its head the divided circle *k*, the silver scale of which is divided directly to

15', and at its lower extremity a hollowed milled disc  $l$  for the purpose of rotating the divided circle by the hand, together with all that its hollow cone bears within it, including the crystal on its holder, when the telescope and vernier have been fixed by  $f$ . A fixing screw  $m$ , working against a clamping ring as in the case of  $f$ , is provided for fixing the circle and all that it carries, quite independently of the fixation of the vernier-circle and telescope, so that either the divided circle with the crystal, or the verniers with the telescope, can be separately either moved or fixed. Moreover, the fixing by  $f$  and  $m$  does not occur directly to the fixed base or feet of the instrument, but to the ring in each case, and this ring is continued horizontally into a narrow V-shaped arm in order to provide a fine adjustment, by a screw working through the basal foot at right angles to the direction of  $f$  or  $m$ . The arm carries a strong spring alongside it, free at the outer end but screwed to the ring at the inner end, and when the adjusting screw pushes the arm, the free end of the spring is pressed against a

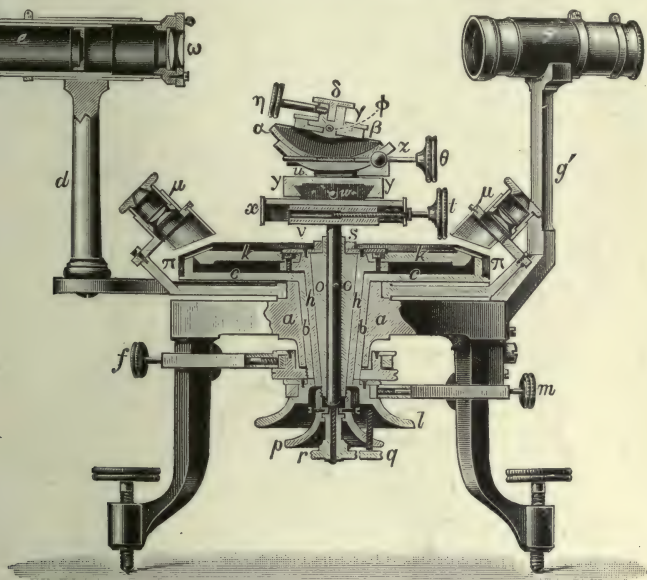


FIG. 21.—Section of No. 2 Fuess Goniometer.

little bracket carried by the foot, and thus fine adjustment is afforded until the spring and arm are forced into contact, and on releasing the screw the arm retrogresses along with it owing to the pressure of the spring. Hence, the divided circle and the crystal carried in rigid attachment with it may be fixed by  $m$ , and the telescope and the pair of verniers which move with it rotated about them; they may then be fixed by  $f$  at any desired point, and the fine adjustment carried out by use of the adjusting screw. Equally well, the telescope and verniers may be fixed by  $f$ , and the divided circle and the crystal which it carries may be rotated instead, by means of the disc  $l$ , or more readily still by a ring  $n$  (Fig. 20) attached below  $l$  by two vertical rods, and eventually fixed in the desired position by  $m$ , and finally adjusted by the adjusting screw.

Within the conical axis  $h$  there rotates still a third one  $o$ , manipulated by the milled disc  $p$  attached to its lower end. This axis is primarily intended for the support of the crystal, which is thus carried separately and not directly by  $h$ , in order that the rotation of the delicately divided circle may be avoided during all the



preliminary adjustment of the crystal, and unnecessary wear and tear of that all-important axis saved. Moreover, the further advantage is secured of rendering the crystal axis very free of movement, not having the weight of the circle to carry except during measurements, and thus enabling the preliminary adjustments to be very

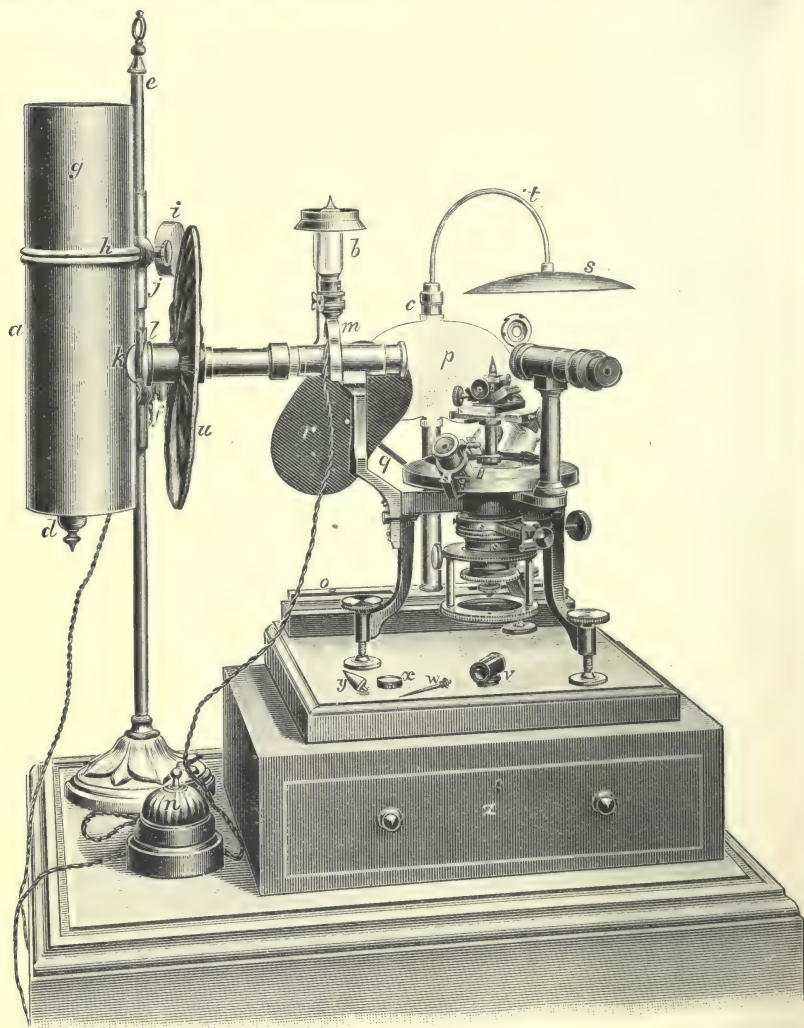


FIG. 22.—No. 2a Fuess Goniometer in Actual Use.

rapidly performed. The crystal axis *o* and the circle axis *h* can be locked together for the measurements either by a simple screw *q* as shown in Fig. 21 (No. 2 model), or by a fixing screw and a fine adjustment screw similar to *f* and *m*, as shown in Fig. 20, the latter being the arrangement on the latest form of this admirable Fuess instrument, model No. 2a, which has been employed by the author throughout his researches, and which is also shown with its accessory fittings in Fig. 22.

The crystal is still not carried directly by the conical axis  $o$ , but at the head of an innermost cylindrical axis, which is keyed to prevent rotation, and the lower end portion of which is narrowed, and provided with a screw thread which gears with a flanged vertically immovable nut terminating below for the purpose of manipulation in a small milled disc  $r$ , the rotation of which consequently causes vertical motion of the crystal axis. The object of this inner axis is thus to provide the crystal with an adjustment for height, so as to bring it to the level of the plane of the optic axis of the telescope and collimator. It may be fixed at this height, if required, by tightening the collar  $s$  by means of a key provided.

The innermost axis just referred to bears the adjusting apparatus at the head of which the crystal itself is carried. This adjusting apparatus consists of two mutually rectangular horizontal movements for centring the crystal, and above them two circular movements in vertical planes also at right angles to each other, for adjusting the tilt of the crystal so as to bring the intersecting edge of any two faces, or the axis of any zone of faces, truly vertical and parallel to the goniometer axis. The two combined pairs of movements enable the edge or zone axis to be brought exactly into the axis of the divided circle of the goniometer. The lower centring movement is manipulated by the traversing screw  $t$ , and the upper one at right angles to the lower by the similar screw  $u$ . Each of these two screws is surrounded by a spiral spring confined between the fixed piece  $v$  or  $w$  (the nut of the screw) and the traversing box  $x$  or  $y$  to prevent "backlash." The fixed piece  $w$  of the upper movement is only fixed as far as regards movement by  $u$ , being rigidly attached on the top of and at right angles to the traversing box  $x$  of the lower movement, with which it therefore moves. On the traversing box  $y$  of this upper centring movement is fixed the cylindrical bed  $z$  of the lower rotatory adjusting segment  $\alpha$ , and on the latter the similar but smaller bed  $\beta$  of the upper segment  $\gamma$ , the circular movement of the two sliding cylinder-segments being effected by the two tangent screws  $\theta$  and  $\phi$ , provided with spring arrangements seen under the segments in Fig. 20, for ensuring perfect contact and no free play. The two segments have a common centre of movement at a height somewhat above the small tabular crystal-holder  $\delta$ , which fits by a little peg in a central vertical boring in the upper segment, in which position it may be fixed by the screw  $\eta$ ; this enables the crystal to be supported at approximately the centre of movement by and at the apex of a little cone of goniometer wax built up on the tabular holder-top, and thus the amount of centring required by the centring screws  $t$  and  $u$  is minimised. The angle of movement of each segment is about  $40^\circ$  on each side of the centre, which is ample to allow of several adjacent zones of faces being measured without re-setting the crystal on the wax. The wax employed is a judicious mixture, generally about two parts to one part, of beeswax and pitch, melted up together and thoroughly blended; when cold it is sufficiently adhesive and soft to permit of ready attachment of the crystal, while being adequately solid not to allow slipping after attachment.

The divisions of the divided circle  $k$  and of the vernier-circle  $c$  are protected by a brass cover-cap,  $\pi$ , attached below to  $c$ , and the scales themselves, which are engraved on silver surfaces inclined (the circle plate being bevelled) towards the observer for convenience of reading, are read through two diametrically opposite glass-covered windows, at the places where the vernier divisions of  $c$  are engraved, by means of a pair of microscopes  $\mu$  carried on suitable arms from a ring fitting loosely round the boss of the fixed table  $a$ . This method of support enables the microscope in either case to follow the vernier divisions; the latter are evenly illuminated by light reflected from a little adjustable mirror,  $\chi$ , and diffused through a thin screen of horn, and each microscope is furnished with an adjustment to the proper focal position for clear reading of the scale and vernier divisions.

The collimator  $g$ , carried by the column  $g'$  in rigid connection with the fixed table of the instrument, is provided with an achromatic lens at the end nearest the crystal, and at the outer end, at the focus of the lens, with one of the four following inter-



changeable signals, each of which is fitted in a separate draw-tube sliding in the outer collimator tube. (1) An ordinary rectilinear slit, provided with an adjustment for one of the jaws, in order to be able to vary the width of the opening by means of

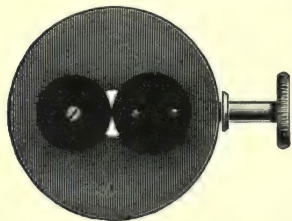


FIG. 23.—The Websky Signal-Slit.

a little traversing screw. (2) A "Websky" slit, shown in Fig. 23, formed by two circular discs arranged in front of a round aperture, and the separation of which can be varied by the movement of one of them by means of a traversing screw, the milled head of which is shown to the right in the figure. This is the form of signal-slit which is practically always employed in the measurement of crystal angles, for it combines the advantages of a narrow central part, the image of which may be readily adjusted exactly to the vertical spider-line of the telescope eyepiece, with broad ends which

transmit much more light than a parallel straight-edged slit narrow enough for accurate adjustment, and consequently affords bright images even from poor or minute faces which would scarcely show the image of a rectangular slit at all. (3) A round pinhole, which is sometimes useful to determine a small deviation of a face out of a zone, or for the study of groups of vicinal faces (adjacent faces only very slightly inclined, that is, nearly parallel, and affording signal-images very close together). (4) A "Schrauf" signal which is sometimes used in preference to (3) in the cases of very brilliant faces, and which consists of two broad rectangular slits arranged crosswise like the diagonals of a square, and with a horizontal and a vertical cross-wire at their intersection in the centre of the field.

It is an advantage to employ in front of the slit an "illumination" tube  $\psi$  as shown in Figs. 20 and 22, consisting of a brass tube slipping over the end of the signal tube and widening towards the outer end, where it carries a condensing lens somewhat larger than the collimator and telescope-objective lenses and the focus of which is the slit, so that the light from the illuminating lamp is concentrated on the latter. The tube has an open rectangular window in its narrower part near the slit, for convenience of rotating a Nicol prism which is provided to slide, when required, in the tube at this part, when it is desired to polarise the light entering the collimator, as during the determination of the refractive indices of doubly-refracting crystals. Longitudinal marks on the Nicol and on the window edge enable the former to be set with its polarising plane in the desired direction, vertical, horizontal, or at  $45^\circ$ .

The observing telescope  $e$  is provided with four interchangeable eyepieces, three of which are positive achromatic combinations magnifying respectively about seven, five, and three times, the last of which is almost always used as being the best combination for affording good lighting of the signal reflections from crystal faces, while still yielding adequate definition and delicacy of measurement. The fourth is used in connection with a lens supported, when required, by a suitable adapter about an inch in front of the objective; this combination furnishes an image which is actually less than the real size of the signal-slit, and is designed for use in those cases where the image afforded by the ordinary eyepiece is very feeble, owing either to the very minute size of the crystal or the particular face, or to the dulness of the face, the concentration of light in such a small image rendering it visible and adjustable to the intersection of the crossed spider-lines when it would be almost invisible and certainly not accurately adjustable if the ordinary third eyepiece were used, which far more than counterbalances the loss of delicacy in the measurement. Each eyepiece carries at the focus of the lens combination, which is adjustable in a draw-tube, a pair of rectangularly crossed spider-lines, mounted in an inner ring adjustable for its position in the tube by four screws; the outer eyepiece tube in its turn slides in the main objective tube so that the telescope can be accurately adjusted for parallel rays,



and when this is achieved the position can be made recoverable at any time by means of a collar, which can be fixed by a tightening screw and which has a V-shaped projection fitting in a corresponding notch in the fixed objective tube, and which is so adjusted that when the eyepiece is pushed home not only is adjustment for parallel rays effected but also the crossed spider-lines are accurately horizontal and vertical.

In front of the objective, which is a similar achromatic lens to that carried by the collimator, there is also attached, by a marginal pin so that it can be rotated out of the way when the telescope is to be used as such for parallel rays, an additional lens  $\omega$  which converts the telescope into a low-power microscope the focus of which is in the axis of the goniometer, and which, therefore, affords the observer a magnified view of the crystal and thereby greatly facilitates the adjustment of the latter, and also enables the reflecting face to be identified by actual observation, the face appearing brilliantly illuminated while the rest of the crystal is relatively dark.

A convenient mode of mounting the instrument, on a mahogany base forming the plinth for a glass case to protect the whole when not in use, is shown in Fig. 22, which exhibits also three essential accessories. These are: (1) the goniometer lamp  $a$ , (2) an intermittent light  $b$  for reading the verniers, and (3) a simple apparatus  $c$  for furnishing a white or black background.

The goniometer lamp is a metallic filament electric glow-lamp of the new type with short thick filament, known as a half-Watt lamp (*per candle power*) and affording 120-candle power on a 100-volt continuous current supply, and in a particularly suitable concentrated form. It is mounted on an arm  $d$  capable of sliding up and down a tall standard  $e$  and of being fixed at the convenient height opposite the lens of the illuminating tube by means of a milled-headed screw  $f$ . The observer is shielded from the light by means of an enveloping vertical copper cylinder  $g$ , supported in a ring  $h$  carried by an adjustable arm similar to that which supports the lamp, and which also is continued on the other side of the standard into a counterpoise  $i$  to facilitate the sliding, and is capable of fixation at the convenient height by means of a screw  $j$ . A circular aperture  $k$   $1\frac{1}{4}$  inch in diameter is cut out of the cylinder at a little more than one-third of its height, and the arm is adjusted so as to bring this aperture exactly opposite the lens  $l$  of the illumination tube, so that the light may fill the latter. A cap carrying a finely-ground glass plate is fitted on the end of the tube, in front of the lens, in order to diffuse the light so as to produce an evenly illuminated signal. The vernier light  $b$  is a small cylindrical-bulb electric glow-lamp of 8-candle power, mounted on a little fitting  $m$  above the outer fixed tube which carries the collimator, and shaded and reflected downwards on to the verniers, the green shade lined with white being removed in the figure in order to reveal the lamp. A switch  $n$  is provided on the mahogany base, to the observer's left, for this lamp requires to be switched off after each reading of the verniers, as the placing of the signal-image reflected from a crystal face, to the cross-wires of the telescope, requires to be carried out in the dark, with no light, that is, except that from the goniometer lamp. For this reason goniometrical observations are either carried out at night, or in a room provided with means of darkening.

The construction of the simple background apparatus will be clear from Fig. 22. For the accurate adjustment, to the cross-wires, of the image of the signal reflected from a crystal face, a dark background is required, while the preliminary adjustment and centring of the crystal by the two circular and two rectangular movements provided for the purpose is best carried out in front of a white background, until the operation is approximately achieved. In order to supply either background as desired, the little arrangement shown at  $c$  in the illustration was devised. It consists of a brass pillar screwed into a bevelled foot-plate, which is adjustable to the most convenient position by sliding in a dove-tailed groove in a heavy metal

base *o*. The pillar carries the fixed white xylonite background *p* in front, and is pierced by an axle at about a third of its height, below the xylonite plate; to the front end of the axle is attached an arm *q* which carries the black ebonite background *r*. The amount of rotation is so limited by a pin and a slot that at one extremity of movement the black background is in position perpendicular to the axis of, and opposite to, the telescope, while at the other it is rotated over so as to leave the white background exposed instead. A thin brass canopy *s* to protect the crystal from scattered overhead light is also loosely attached to the top of the pillar by a curved rod *t* rotatable in a socket in the pillar-head, so that it may be turned out of the way when reading the verniers. The other accessories shown in Fig. 22 are the screen *u* of thick folded green silk over a circular wire frame, for screening off the light issuing from the aperture *k* from the observer's eye; the Becker fitting *v*, the adjusting needle *w*, and glass-plate mirror *x*, the use of all three of which will be explained in the next section; and a second crystal-holder with its wax cone *y*. There is also a drawer *z* in which accessories, note-book, crystals in their miniature bottles, or other articles required may be stored.

**Adjustment of the Goniometer.**—Before proceeding to any measurements of crystal angles with the instrument it is essential that it should be carefully adjusted. For this purpose the following series of operations should be carried out in the order named, as originally given by Websky.

(1) The eyepiece to be employed, preferably the one magnifying about three times, is first adjusted, as regards the position of the draw-tube carrying the positive achromatic lens combination within the outer tube carrying the crossed spider-lines, until the latter are clearly focussed. The eyepiece is then inserted in the telescope tube and its position varied until the whole telescope is adjusted for parallel rays, as indicated by the clear focussing of some very distant object.

(2) A special holder, *w* in Fig. 22, resembling the crystal holders in its mode of attachment to the goniometer, but carrying a vertical needle instead of a tabular head for the attachment of a wax cone, is inserted by its peg in the central hole in the top of the crystal-adjusting movements, and adjusted by the latter vertically in the axis of the goniometer. The eyepiece is then rotated, if necessary, until one of the spider-lines is parallel to the needle as viewed through the micro-telescope, the lens  $\omega$  (Fig. 20) in front of the objective having been rotated into position. It may now happen, after full use has been made of the centring movements and the needle remains apparently immovable as the goniometer axis carrying it is rotated, that the images of the needle and the vertical spider-line are not coincident, but only parallel. They must now be brought into coincidence, and this can be done either by moving the spider-lines horizontally or by an adjustment of the setting of the pillar which supports the telescope. The crossed spider-lines are mounted in an annular frame which slides with some little play in the main eyepiece tube, and is adjustable from outside by four diametral screws, a horizontal pair and a vertical pair; the two former enable the required adjustment to be made. But when the adjustment required is more than a very minute amount, and involves displacing the intersection of the spider-lines from the optic axis of the telescope, the author prefers to effect the adjustment of the whole telescope, which is really also the



more correct thing to do. For this purpose an addition has been made to the instrument as furnished by Fuess, of three little adjusting screws passing from below through the arm which carries the pillar, and pressing up against the circular base of the pillar near its periphery. Starting with these screws not in action, and the base firmly screwed to the arm by the stout central fixing screw, on observing that the vertical spider-line lies to one side of the needle, it is easy to bring the little screw on the opposite side, or two of the three screws, into action while slightly releasing the fixing screw, until the needle and spider-line are coincident, and subsequently to tighten up the fixing screw again. Probably the latter operation will have very slightly again displaced the spider-line from coincidence with the needle image, and one or two closer and closer approximations may be necessary before final adjustment is achieved.

(3) A small circular plate of glass provided with the instrument, with surfaces ground truly plane and parallel, and mounted in a circular frame,  $x$  in Fig. 22, with peg for insertion in the hole in the top of the adjusting movements, is next adjusted approximately parallel to the axis of the goniometer, and then left as nearly as can be judged perpendicular to the axis of the telescope. A small fitting carrying another small plate of glass arranged at, or adjustable to,  $45^\circ$  to the axis of the telescope, is now fixed in front of the eyepiece, and a lamp arranged to reflect light from the inclined glass plate through the telescope to the circular glass plate on the goniometer axis, so as to obtain both a direct view of the crossed spider-lines by scattered light and their reflection in the parallel glass plate. An excellent little fitting for the purpose is now supplied by Messrs. Becker of Hatton Garden. It is shown at  $v$  in Fig. 22, and more clearly in Fig. 24. It screws on to the end of the cap-tube in front of the eyepiece instead of the usual cap with eye-hole, and the inclined plate is carried in a little tube fixed transversely to the very short tube bearing the screw thread just referred to; this transverse tube is closed at one end, at the other carries a lens to concentrate the light from the lamp on the glass plate, and is pierced with a hole in front of the centre, through which the observer looks instead of through

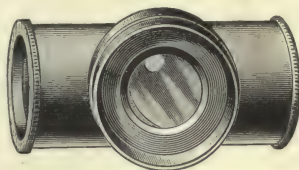


FIG. 24.—The Becker Transparent Eyepiece-Mirror.

the usual eyehole. The illumination of the spider-lines afforded by this fitting is excellent, and enables the adjustment to be very rapidly carried out. The parallel glass plate should now be rotated in order to see if it is exactly parallel to the axis of the goniometer, as indicated by the images of the spider-lines reflected from the two surfaces of the plate occupying in turn exactly the same position in the field, and if this is not the case it should be adjusted so that it is so. If now the intersection of the spider-lines as reflected is not quite coincident with the intersection as seen directly, it should be made so either by raising or lowering the spider-line fitting by its adjusting screws, or by using the adjusting screws at the base of the telescope pillar as already described for adjustment (2).



The axis of the telescope will then be truly normal to the plate and perpendicular to the goniometer axis. The horizontal spider-line should also be exactly perpendicular to the goniometer axis and coincident with its own reflected image, and should appear to remain so, although both spider-lines and their intersection will traverse the field (moving at right angles to the goniometer axis), when either the plate or the telescope is slightly rotated about the goniometer axis. When finally satisfied that the adjustment of the spider-lines, eyepiece, and the whole telescope is perfect, the collar of the eyepiece should be brought along so that its V fits the notch in the outer telescope tube, and fixed there by the clamping screw, so that the adjustment may be at once recovered whenever this eyepiece is again replaced after temporary removal. The fitting in front of the eyepiece is now removed, and the ordinary cap with hole substituted.

(4) The small circular-hole signal is next inserted in the collimator, and the telescope rotated into the same straight line with the collimator so as to observe the hole; the latter is then brought to sharp focus by movement of the signal tube in the outer collimator tube, and the latter adjusted, by means of the adjusting and fixing screws by which its supporting column is attached to one of the legs of the tripod, so that the centre of the image of the signal-hole lies on the horizontal spider-line. The Websky and the straight-edged signal-slits may next be inserted in turn in the collimator tube, and moved about therein until focussed clearly by the telescope in the truly vertical position and symmetrical to the crossed spider-lines of the telescope. After this adjustment is achieved, in the case of each of the three signals, the sliding collar should be moved up so that its projecting V fits into the notch of the collimator tube, and fixed there by the clamping screw, so that when any one of the signals is required it can at once be pushed into position. The Schrauf diagonal slit and cross-wire signal should next be inserted in the collimator tube, and the intersection of the cross-wires brought into coincidence with that of the spider-lines of the telescope by the four traversing screws of the signal itself, provided for the purpose, after which in this case also the sliding collar may be fixed. This signal may be advantageously left in for the adjustment of the other eyepieces than the one magnifying three diameters already adjusted, after which it should be replaced by the Websky signal, when the goniometer will be quite ready for use in crystal measurement.

For the measurement of crystal angles at higher temperatures than the ordinary and the determination of the minute change of angle brought about by rise of temperature, which may amount to only a few seconds, a larger horizontal goniometer reading to seconds is constructed by Fuess, the No. 1a. This instrument, however, and its use in higher temperature work, will be described in Chapter XXVI. It is also eminently suitable for the determination of refractive indices. It is not so handy, however, for crystal-angle measurements at the ordinary temperature, in which the extra refinement beyond half-minutes is of no advantage; for analogous angles on the very best crystals of the same substance

differ by as much as a whole minute, owing to slight disturbance of the conditions during deposition. The instrument No. 2a is undoubtedly the goniometer *par excellence* for crystal-angle work at the ordinary temperature.

A simpler and much cheaper form of horizontal-circle goniometer suitable for student use is also now furnished by Fuess, which is quite an efficient instrument although not so delicate as the No. 2 or 2a models, and not fitted with such excellent means of ready and accurate adjustment.

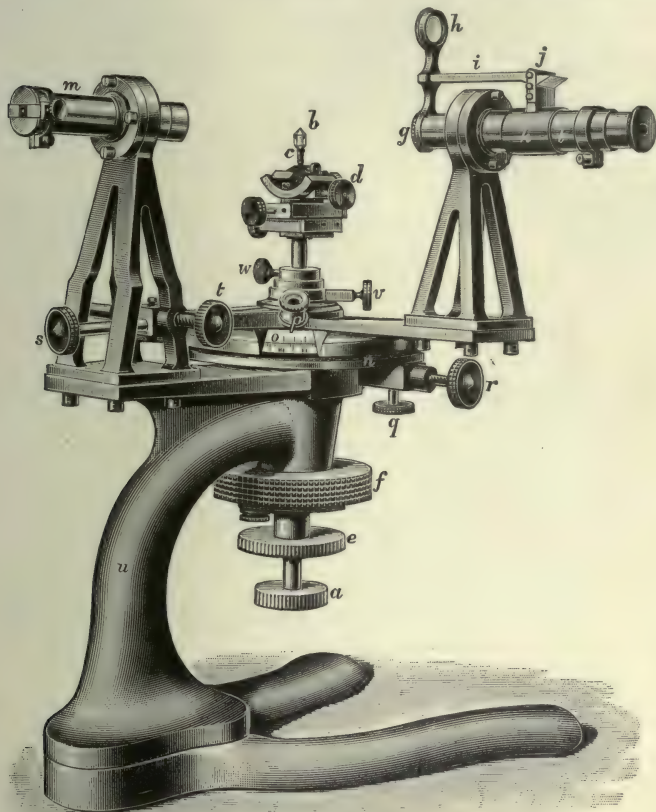


FIG. 25.—Troughton and Simms Horizontal-circle Goniometer.

**Troughton and Simms Goniometer.**—An accurate form of horizontal-circle goniometer constructed by Messrs. Troughton and Simms is shown in Fig. 25. Its principle is the same as that of the Fuess instrument.

The lowest *a* of the three milled heads shown under the circle-cone is rotated to raise or lower the crystal *b*, and its holder *c* and adjusting apparatus *d*; the middle one *e* rotates the latter with the crystal, during adjustment, and the large upper milled head *f* is used to rotate the circle. A novel feature, due to Sir Henry Miers concerns the lens in front of the objective of the telescope; for instead of the usual

one rotatable merely in or out of the field, in order to convert the telescope into a microscope while observing the crystal itself, this lens  $g$  and a second one  $h$  are mounted at the extremities of a short cross-piece carried by a horizontal bar  $i$ , the whole forming a T-piece which is capable of swinging about a bearing  $j$  carried by a short tube  $k$  sliding along the outer telescope tube  $l$ . When arranged as shown in the figure, the first lens  $g$  is in the usual position for crystal observing purposes, but when the T-piece is swung back the second lens  $h$  is brought in front of the eyepiece, and serves to follow up the signal-image reflected from any particular face, until it becomes replaced by the image of the illuminated face itself, as the lens is drawn away from its position close to the eyepiece towards the eye. This device is of use when it is doubtful from which of several illuminated and very closely adjacent faces an image is proceeding, and was invented for the study of such vicinal faces.

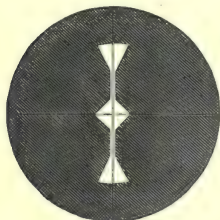


FIG. 26.—Miers Signal-slit.

A modification of the Websky slit was also introduced by Miers, the nature of which will be clear from Fig. 26.

In Fig. 25 the collimator is marked with the letter  $m$ . The circle is indicated by  $n$  and its vernier by  $o$ ;  $p$  is the reading microscope,  $q$  the fixing screw, and  $r$  the fine adjustment of the circle. The fixing screw for the telescope is marked  $s$  and the fine adjustment  $t$ . The whole is supported on a convenient form of rigid stand  $u$ . The crystal-holding and adjusting axis may be fixed to the circle by the screw  $v$ , and  $w$  is a clamping screw for fixing the innermost steel axis after it has been raised or lowered by the milled head  $a$ .

### Relative Advantages of Horizontal- and Vertical-Circle Goniometers.

—The chief advantages which the horizontal-circle form of goniometer possesses over the form with vertical circle are the following three: (1) the crystal is less liable to displacement during the measurements, by the yielding of the wax cone of support; (2) larger crystals can be used with greater convenience, largely owing to the greater rigidity of the wax support; (3) the large amount of possible movement of the telescope, nearly  $360^\circ$ , enables the instrument to be employed for the determination of refractive indices, as well as for the measurement of crystal angles. At the same time the vertical-circle instrument possesses the following three relative advantages, namely: (1) the inclined telescope (if one be employed) is easier to observe down than the horizontal one; (2) it is easier to read the circle, the graduations being on the edge of the vertical disc; (3) the milled heads for rotation of the various axes, and possibly also those of the adjusting and centring screws, are somewhat more accessible. On the whole, however, the author vastly prefers the horizontal-circle instrument for refined work. But for teaching purposes a relatively much cheaper instrument can be constructed on the vertical-circle principle, and the best, a very efficient, form of this goniometer will next be described.

**The Miers Student's Goniometer.**—This is a much less costly form of goniometer constructed on the vertical-circle principle by Messrs. Troughton and Simms to the designs of Sir Henry Miers, and is eminently suited for the use of students. The observation by telescope and collimator is replaced, in the simple form of the instrument recommended, by the use of a mirror to reflect the image of a distant signal-slit, placed



in an otherwise darkened window, and which is likewise caused to be simultaneously reflected from the crystal face, the reading of the circle being taken when the two reflections are brought into coincidence to an observer looking vertically downwards on to crystal and mirror from above. A general view of the instrument is given in Fig. 27, and Fig. 28 will assist in explaining its principle.

In the latter illustration M represents the fixed mirror, I the incident light originating from the signal-slit cut in a window shutter at not less than 20 feet from the mirror, *ab* and *bc* two adjacent faces of the crystal, the edge *b* between them being arranged so as to be parallel to the mirror and the face *ab* so as to afford a reflected image of the signal-slit. This image is then brought, by rotation of the crystal, to coincide exactly with the similar image of the signal-slit reflected in the mirror, and the crystal being so small compared with the size

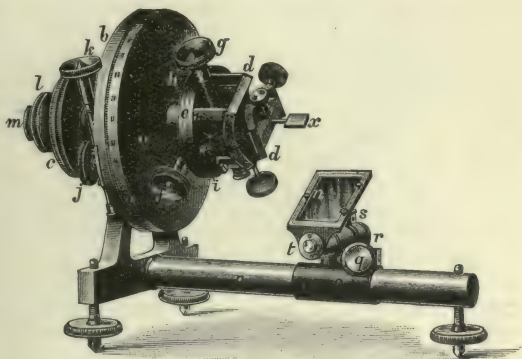


FIG. 27.—Miers Student's Goniometer.

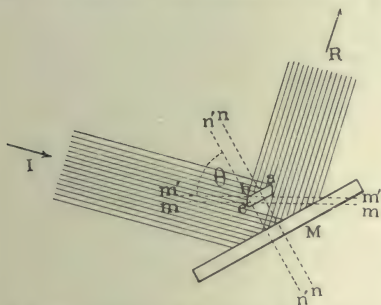


FIG. 28.—Principle of Student's Goniometer.

of the mirror there is no difficulty in seeing both images at the same time. When coincidence is attained a reading of the circle is taken. The crystal is then further rotated until the image reflected from *bc* is similarly brought to coincidence with the mirror image, and another reading of the circle made. The difference of the readings is the angle required, namely  $\theta$ , that between the normals *nn* and *mm* to the two faces. For if we draw these normals to the faces *ab* and *bc* respectively at their centres, and then move them parallel to themselves until they occupy the positions *n'n'* and *m'm'* in which they intersect at the adjusted edge *b*, the centre of rotation, then on rotation of the crystal from the position shown in the figure, when the image of the signal reflected by the face *ab* is adjusted, to that when the image from *bc* is similarly adjusted, the normal *m'm'* moves through the angle  $\theta$ , that is, until it becomes identical with that occupied under the conditions represented in the figure by *n'n'*. This angle  $\theta$  is thus the required crystallographic angle between the normals to the two faces *ab* and *bc*.

The actual construction of the instrument will be clear from Fig. 27. The circle

*a* is vertical and divided directly on the periphery to half-degrees, while a vernier on the fixed disc *b* against which the circle rotates enables the latter to be read to one minute; it is rotated by the large milled head *c*, and is kept in close contact with the fixed disc by means of a circular steel spring inserted between *c* and the bearing of the axle. The crystal is carried at the end of an adjusting arrangement *d* and centring apparatus *e* on the same principle as that of von Lang on the Fuess instrument, namely, two mutually rectangular centring movements and two circular adjusting movements likewise arranged at right angles. The centring movements are of different construction from those of Fuess, each depending on the movement of a circular plate by a screw *f* or *g*, about a pin *h* or *i* passing through the disc near the periphery into a second similar disc, and with the aid of a boss which is kept pressed up against the screw by a spring piston on its other side in the same straight line as the screw. The crystal is thus moved along two circular arcs crossing each other at right angles, and to which the directions of the two screws *f* and *g* are tangential, which arrangement serves the same purpose of centring as if the arcs were straight lines. The discs are kept in close contact by a pin working in a circular arc-shaped slot at the opposite side of the disc to the axle pin, a spring being confined between the broad head of the pin and the outer disc to effect the essential close contact. The cylindrical adjusting segments are similar to those of the Fuess goniometer.

The circle is provided with a fine adjustment, the screw *j* clamping the divided rotatable circle to the fixed circle *b*, and *k* being the fine adjustment screw which is subsequently brought into operation. The milled head *l* turns the centring and adjusting piece with the crystal, and the smaller outer milled head *m* locks that piece and all that it carries to the divided circle.

The mirror *n* is carried above a tube *o* sliding on the basal cylindrical bar *p*, in such a manner as to be capable of adjustment in two vertical and mutually rectangular planes. The tube *o* can be clamped anywhere along the bar *p* by the fixing screw *q* of a tightening collar. A short column rises from *o* carrying a similar but somewhat narrower tube *r* at right angles to *o*, and provided with a similar tightening collar at *s*. Within this a cylinder slides, but is keyed so as to be incapable of rotation, and may be fixed at any position by *s*; to one end of the cylinder the mirror is attached by means of the capstan-headed screw *t*, which can be loosened so as to allow the mirror to be adjusted by rotation and then screwed home. The mirror is thus capable of four movements, namely, rotation about *t* and also of *o* about *p*, these two rotations being in planes at right angles; also two perpendicular rectilinear movements by the sliding of *o* along *p* and of the cylinder in *r*. The adjustment of the mirror is achieved once for all by setting it parallel to the axis of the goniometer, while the screw *t* is loosened and with the aid of the signal-slit in the window and a small disc of truly plane and parallel-surfaced glass, mounted instead of a crystal at the end of the crystal-adjusting movements, as described for the adjustment of the Fuess goniometer. The screw *t* is then finally fixed, and the other movements employed until the mirror is in the best position for seeing the simultaneous reflections from a crystal and the mirror, when the clamping screws should be tightened.

A similar instrument with an equally accurate circle but with a simpler crystal-adjusting apparatus of the type originally used by Wollaston, the inventor in the year 1809 of the reflecting goniometer, is also constructed by Messrs. Troughton and Simms at a considerably lower cost, and is shown in Fig. 29. The construction of the two simple adjusting movements *d'* will be quite clear from the illustration; two rods *u* and *v* at right angles to each other, one of them, *v*, carrying the crystal-holder *x*, can be rotated in bearings by milled heads *y* and *z*,

and serve for the adjustment of the crystal edge, that is, of the pair of faces intersecting in the edge. The centring is achieved by means of the slotted bar  $e'$ , which is capable of being clamped to the circle when the crystal is centred, by the milled head  $\alpha$  shown in the figure, and which carries the adjusting movements at the end of an elbow  $\beta$  springing from its inner end.

In using either form of this goniometer the observer looks down from above on to the crystal and mirror, but with the eye accommodated for distance, so as to focus sharply the images of the window-slit reflected from the crystal face under observation and from the mirror. In order to adjust the crystal so that the two images exactly coincide, it is convenient to cut off half of the light falling on the mirror from the signal-slit, by means of a little cardboard screen placed on the table in front of the goniometer, of the right height to perform this function while allowing the light to fall freely on the crystal. By moving the screen about over the table, part or all of the signal reflection from the mirror can be cut off, so as to distinguish it plainly from the crystal reflection, and when half only is cut off it is easy to make the signal-image from the crystal form an exact prolongation of the remaining half, and in this way obtain a better coincidence than by complete overlapping, as it is difficult to distinguish the separate edges when near coincidence. When this coincidence has been thus attained the reading of the circle is taken.

If it be found inconvenient to employ a window-signal, for instance because the room is very small, a collimating arrangement of a small slit in an opaque disc placed at the focus behind a large lens of about five inches focal length, the latter being brought close to the goniometer and the former illuminated by a table lamp, serves admirably.

The author finds it better to have for use with this arrangement a separate mirror-fitting with the mirror raised higher, nearer to the crystal, than the ordinary one, as the two images are then better covered and illuminated by light from the central part of the lens.

By the addition of a collimator  $\gamma$  and telescope  $\delta$  to this instrument, as shown in Fig. 30, it can be converted into an efficient goniometer more or less comparable with the Fuess instrument at less than half the cost. The levelling screw at the end of the bar  $p$  is temporarily removed, while the mirror-fitting is replaced by one  $\epsilon$  carrying the telescope and collimator, after which the levelling screw is again fixed in position.

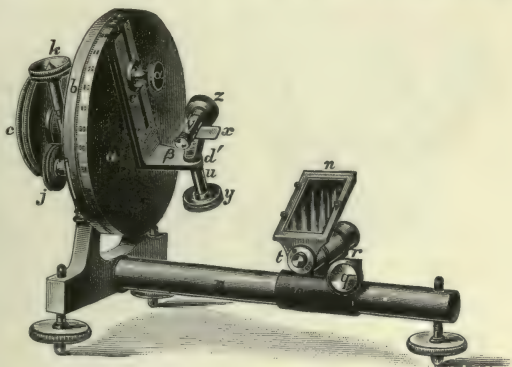


FIG. 29.—Simple Form of Studnet's Goniometer.



The sliding tube  $\eta$  which carries this fitting may be clamped at the proper position by two screws  $\theta$ , which tighten a pair of split collars.

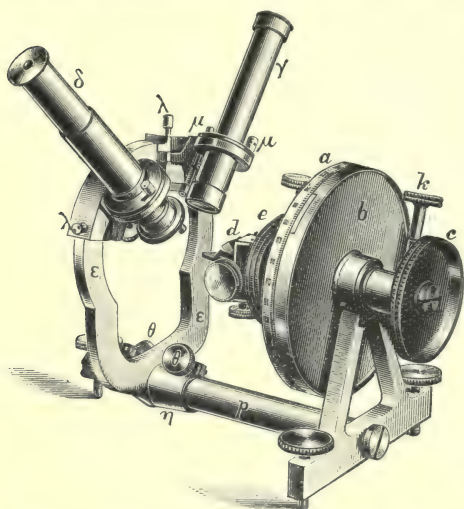


FIG. 30.—Miers Student's Goniometer with Telescope and Collimator.

The telescope  $\delta$  and collimator  $\gamma$  move over a vertical circular arc of rather more than a semicircle, and they may be fixed at the suitable positions by means of screw clamps. Adjustment screws  $\lambda$  and  $\mu$  are provided which enable the optical tubes to be adjusted exactly in the vertical plane and directed truly to the axis of the instrument.

A students' goniometer of somewhat similar construction to the Miers instrument represented in Fig. 29 is constructed by Messrs. Steward to designs by Dr. G. F. Herbert Smith. It is shown in Fig. 31.

The mirror in this instrument is attached to the ball of a ball-and-socket joint, so that it is adjustable in any direction. The socket is split, and a screw linking the

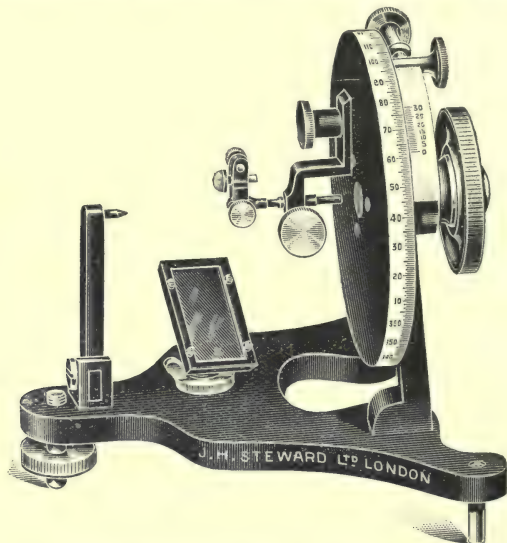


FIG. 31.—Herbert Smith's Modification of Miers' Student's Goniometer.

halves enables it to grip the ball firmly. The pillar carrying the socket passes through a split collar slightly tapering in shape, which may be clamped by means of a butterfly

nut; when released the mirror may be adjusted to the requisite distance from the axis of the graduated circle. The scale of the latter is silvered, and divided into half degrees, which with the aid of the vernier also provided may be subdivided into single minutes of arc, as in the case also of the Miers student's goniometer.

The method of adjusting the crystal presents some novelty. The crystal-holder itself is of the usual type, a small circular plate at the end of a pin, which can be clamped in its socket by a screw. The short arm carrying the clamping piece is hinged at its lower end, and can itself be firmly clamped by a screw forming the pin of the hinge. The co-ordination of these two motions in varying proportions suffices for the adjustment of an edge on the crystal, parallel to the axis of the circle, and enables one half of the crystal to be measured without readjustment on the wax. The hinge referred to is attached to a horizontal pin passing through a split collar, which may be tightened by means of a screw. This collar is carried on an arm, which is bent away from the plane surface of the circle for convenience of access to the head of the screw operating it. The arm in turn is pivoted at a point on the flat face of the graduated circle about 3 cm. from the centre, and the central line of the collar, and therefore of the pin passing through it, is of precisely the same length; consequently the rotation about the pivot carries the central line of the horizontal pin through the axis of the circle. The arm may be fixed by means of a screw forming the pivot. To prevent the arm dropping on release of the screw, the latter bears on a small spring surrounding it, which is carried in a collar fixed to the arm. This second pair of movements forms the means of adjusting the crystal into the line of the axis of the graduated circle, while the lengthwise movement of the horizontal pin within its collar, when released, permits of the setting of the crystal above the mirror. To facilitate this adjustment a pointer (on the left in Fig. 31) is provided, which can be swung out of the way when not needed, and at once brought back to position by turning it until its arm comes up against a stop.

In Chapter XXVII. some further forms of goniometer having two and three circles will be described. The two-circle theodolitic method of goniometry has recently come into considerable use, largely due to the influence of Prof. V. Goldschmidt of Heidelberg, but is much more suitably discussed at a later stage.

## CHAPTER IV

### THE MEASUREMENT OF CRYSTAL ANGLES, PRACTICALLY EXEMPLIFIED ON A CRYSTAL OF POTASSIUM SULPHATE, AND CONSTRUCTION OF THE STEREOGRAPHIC PROJECTION

THE most practical method of illustrating the mode of measuring the angles of crystals will be to take an actual example, from among the numerous crystals of high perfection measured by the author. During the process the regular plan of symmetry on which the crystal is built up will be elucidated, and the mode of graphically representing the results in a "spherical" or "stereographic projection" explained. The example chosen is a crystal of potassium sulphate, a salt already referred to in the first chapter and illustrated in Figs. 1, 2, and 3, and so common and cheap, while exceptionally pure, as to be within the reach of every one. In preparing similar suitable crystals for measurement, in order to repeat these sample measurements as a first practical exercise in goniometry, the general rules given in Chapter II. must be followed, especial care being taken that the solutions, when cooled to the ordinary temperature, shall not be more than the slightest amount supersaturated. The normal sulphate of potassium,  $K_2SO_4$ , is only sparingly soluble in water, 10 grammes dissolving in 100 cubic centimetres of water at the ordinary atmospheric temperature, so that solutions stronger than ten *per cent.* cannot be made at this temperature, and even at  $100^\circ$  C. potassium sulphate is only soluble to the extent of 26 grammes *per* 100 c.c. There is a great risk of obtaining long irregular prisms unsuitable for measurement by cooling from a solution saturated at  $100^\circ$ , but a solution just slightly supersaturated at the ordinary temperature, say by solution of about 12 grammes of the salt in 100 c.c. of boiling distilled water and slow and spontaneous cooling, will generally be found to deposit at least one or two well-developed crystals of the type shown in Fig. 32 (which is a repetition of Fig. 1, made here for the reader's convenience), on leaving the solution to continue to cool and deposit its excess of salt during the night, under the protected conditions described in Chapter II. One or two crystallisations may be necessary to secure really excellent crystals, and sometimes such solutions remain thus slightly supersaturated for several days before crystallisation ensues, but with a little perseverance good crystals will eventually be



obtained. The solution will probably be in the metastable condition and require to have its crystallisation started by means of a minute crystal of the salt falling into it from the air, as explained in Chapter II. For both potassium sulphate and its isomorphous analogue, ammonium sulphate, which would almost equally well start the crystallisation, are very common salts, and germ crystals of them are probably floating in the air of every laboratory.

Having thus secured a satisfactory crop of small crystals and stored them in a miniature bottle, properly labelled as described in Chapter II., one of the best may be selected, of the small size there recommended and which may be as much as three millimetres across the widest part in the case of the salt under consideration. Such a crystal will afford very similar measurements to those obtained by the author with the example now to be dealt with.

**Example of General Procedure for Measurement of a Crystal Angle.—**

It will be evident from the first cursory inspection that the broad face labelled in Fig. 32 with the letter *b* is an important plane of the crystal, and that the smaller faces *a* and *c* are approximately perpendicular to this face *b* and to each other. It will, therefore, be advisable to commence operations by measuring the angles between the faces *a* and *b*, between *a* and *c*, and between *b* and *c*, in order to ascertain whether these angles are really exactly  $90^\circ$ , in which case the three planes will probably be planes of symmetry. Beginning with *a* and *b*, the crystal is attached to the little wax cone of the crystal holder of the goniometer by one of the *c* faces, taking care not to soil by contact

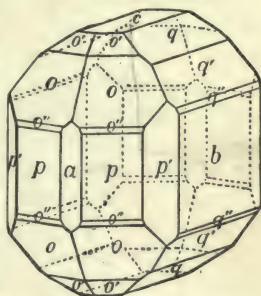


FIG. 32.—Potassium Sulphate Crystal.

with the wax more than a small part of that face. There is scarcely any soiling if the wax be properly made and not too new. The intersection of *a* and *b*, imagining the faces extended so as to meet, instead of the edge being blunted by the intermediate faces, will thus be parallel to the goniometer axis, that is, vertical if the Fuess or other horizontal-circle goniometer is being employed, or horizontal when the Miers student's goniometer is used. The crystal-holder should then be fixed in its socket in such a position that the broad *b* face is parallel to the tangent screw of one of the two adjusting movements. The telescope should be fixed at somewhat more than a right angle from the collimator if the former instrument is being used, and the inner axis carrying the crystal should be left free to move easily and independently, by unclamping it if necessary from the circle. The crystal should first be centred, with the micro-lens in position, by means of the two centring movements and the milled head which effects the raising or lowering of the axis. The inner axis is then rotated until one of the faces, say *b*, is brought into the position from which a reflection of the Websky signal-slit of the collimator may be expected to be visible in the telescope, as indicated by the brilliant illumination of the face itself as seen through the micro-telescope. If the setting on the

wax has been fairly true to that intended, the *b* faces having appeared perfectly vertical when the crystal has been rotated so as to bring the plane of those faces parallel to the axis of the micro-telescope, that is, so as to enable them to be seen in profile, the image of the signal will probably be visible, either at once or on slight rotation of the axis, although most likely it will not be symmetrical to the horizontal spider-line. If this be so, the image can be brought into such symmetrical adjustment by rotation of the tangent screw of the adjusting movement at right angles to the face. If it be not so, the image is probably just vertically out of the field, and the micro-lens had better be temporarily placed in position again while the tangent screw is worked so as to see which direction of rotation brings about a better general illumination of the face, and then adjusted for the maximum illumination; on again removing the micro-lens the signal image will be visible and can be readily adjusted further to the required symmetrical position with respect to the horizontal spider-line.

Having thus adjusted the face *b*, a precisely similar adjustment must be carried out for the face *a*, this time with the aid of the other tangent screw.

If the Miers goniometer without telescope is being used, it is only a question of adjusting the ends of the elongated oblong image of the window-slit, reflected from the crystal face, to coincide exactly with the ends of the image reflected from the mirror. The object is even better attained if a little transverse bar be laid across the centre of the slit, as a mark by which to adjust the image into coincidence.

On reviewing the image from *b*, if the crystal has been arranged so that this face is strictly parallel to the adjusting movement, its adjustment will have remained unimpaired. But this is only attainable by a rare chance, and in general the image will have been slightly displaced from the adjusted position. A partial turn of the tangent screw should suffice to readjust it, and then the image from *a* should be again examined, any necessary slight correction of its adjustment made in the same way, and thus after one or two closer and closer approximations the two faces should be obtained in simultaneously perfect adjustment. The operation will be the simpler, the readjustments being the slighter, the closer the setting of the face *b* to parallelism with the tangent screw has been. After thus accomplishing the "adjustment of an edge," as the operation of adjusting two faces is technically called, a finishing touch should be given to the centring of the crystal, swinging the micro-lens of the telescope into position for the purpose; after this is achieved everything is ready for the actual measurement.

The result of these preliminary operations is that the crystal is truly centred to the common intersection of the three axes of the goniometer-circle, collimator, and telescope, and that the faces *a* and *b* are strictly parallel to the goniometer axis, while also they are precisely perpendicular to the plane of the axes of the collimator and telescope and therefore also to the plane of the circle. On rotation of the circle, which

carries the crystal with it whether the inner crystal axis is locked to it by the fixing screw or not, it will be obvious that when each of the two faces in turn is brought into the position at which the reflected image of the signal-slit is symmetrical to the crossed spider-lines of the telescope, it is then situated perpendicular to the imaginary straight line bisecting the angle between the axes of the collimator and telescope and lying in the same horizontal plane with those axes, in accordance with the optical law of reflection that the angles of incidence and of reflection are equal. In other words, the normal to each face in turn is brought into coincidence with the bisectrix in question, and thus the angle through which the crystal has been rotated is the angle between the normals to the two faces.

The conditions will be rendered clear by Fig. 33, in which T

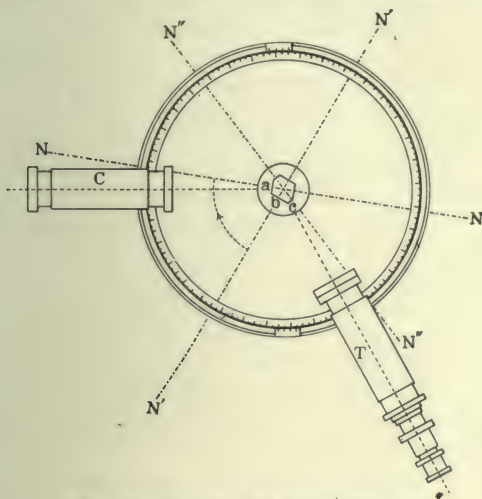


FIG. 33.—Principle of Reflecting Goniometer.

represents the telescope and C the collimator; *a* and *b* are the two crystal faces, the angle between which is first to be measured, *c* is a third face, and *N*, *N'*, and *N''* are their respective normals. *N'* is also the direction of the bisectrix of the angle between the telescope and collimator, the face *b* being adjusted. The interfacial angles as drawn are other than  $90^\circ$  in order to render the illustration as general as possible, although in the case of potassium sulphate the angle  $ab = 90^\circ$ . It will be obvious that the angle through which rotation has been effected, during the successive placing to the eyepiece spider-line of the images of the signal reflected from the faces *a* and *b*, is the angle between *N* and *N'*, indicated in the diagram by the dotted arc. This is the angle required to be measured, for it is much more convenient to consider as the crystal angles the angles between the normals to the faces, rather than the actual angles of intersection of the faces themselves; for they are the supplements of the latter angles, and besides



being in general the smaller, not exceeding  $90^\circ$ , and therefore the more conveniently recorded of the two supplementary angles, they are the angles directly employed in the stereographic projection and graphical representation of the crystals, as well as in the calculation of the crystal elements. Similarly the goniometrical angle between the faces  $b$  and  $c$  is that between the normals  $N'$  and  $N''$ , for the latter in its turn has to be brought into the position now occupied by  $N'$ . The size of the crystal relative to that of the goniometer is much exaggerated in the diagram for the sake of clearness.

Before making the actual measurement of the angle between any two faces thus adjusted, the circle and crystal axes should be clamped together by the fixing screw provided, so that no relative movement may occur during rotation. It is naturally convenient to take the circle readings in descending order, and therefore to bring first the left-hand face,  $a$ , into the position shown for  $b$  in the figure, perpendicular to the bisectrix  $N'$ . Supposing the Fuess goniometer (or similar horizontal goniometer of Troughton and Simms) to be used, as in the case of the author's measurements of potassium sulphate, in placing the image of the Websky signal to the vertical spider-line the dark background should be employed and the vernier light switched off, leaving the room in darkness except for the goniometer lamp in front of the illuminating tube, and which is closely shaded except opposite the condenser of the latter by the copper cylinder. The narrow central part of the signal-image is then to be made coincident with the vertical spider-line, the preliminary adjustment having already arranged the image symmetrical to the horizontal spider-line. The signal-slit should have been once for all previously adjusted so that the narrow central part is just sufficiently wide to enable the vertical spider-line to be clearly defined within it, the curved edges of the image just overlapping (clearing) the spider-line to an equal minute amount on each side.

The circle reading for the face  $a$  may then be taken, the vernier lamp being temporarily switched on for the purpose. A difference of one minute of vernier reading will be so clearly perceptible as to bring the vertical spider-line into contact with, or even slightly to pass, one of the edges of the image. The vernier lamp should then be switched off again, and the circle and all that it carries, including the crystal, rotated by the large milled head or ring until the image of the signal-slit from the second face  $b$  is similarly adjusted, as actually shown in the figure, symmetrically to both spider-lines, when another reading may be taken in the same manner. The difference of the two readings is the required angle between the normals to the two faces. During the rotation from the position for the first image to that for the second, it is usually advisable to slip the micro-lens into position in front of the objective, in order that one can observe the crystal throughout and see when the approximate position for the second image is arrived at by the brilliant illumination of the face which then occurs, and at the same time to verify that it is really the desired face which is furnishing the signal-image. The micro-lens is then again slipped off during the observation and final placing of the image itself.

**Actual Observations with the Example chosen, Potassium Sulphate.**

—The result of the measurement of the angle between the faces *a* and *b* of our potassium sulphate crystal is to prove that the angle is, as surmised, exactly 90° 0'. The next fact that is observed is the very important one that the adjustment of these two faces has automatically adjusted quite a number of other faces. During the rotation from *a* to *b*, if the micro-lens were in position, the intermediate faces to the right of *a* marked in Fig. 32 with the letters *p* and *p'* would be seen to be brightly illuminated in turn, and if the micro-lens were pushed aside the corresponding image of the signal-slit in each case would be seen to be symmetrical to the horizontal spider-line, and a reading of the circle could be taken when each was also brought by the rotation into the position symmetrical also to the vertical spider-line, just as accurately as in the cases of *a* and *b*. Moreover, after passing the image from *b*, and thus completing the first quadrant, it would be found that two similar faces *p'* and *p* would be met with in the second quadrant in the reverse order, that is, symmetrically placed with respect to *b*, and that at the position exactly 180° from *a* and 90° from *b* we should find a face parallel to our original *a* face. Still proceeding through the third quadrant, we should discover two more intermediate faces *p* and *p'*, then a face parallel to our original *b* face, at exactly 180° from that face and at the 270° 0' graduation of the circle. Finally, rotating on through the fourth quadrant, we should discover a fourth pair of *p'* and *p* faces, and eventually arrive at our original *a* face itself again, at precisely the original circle reading of 0° 0' (which is the same as 360° 0') if there had been no slipping of the crystal on the wax.

The following actual measurements were obtained by the author for the crystal of potassium sulphate shown in Fig. 32. The faces marked with an asterisk are those of the right-hand front quadrant in the figure, the asterisked faces *a* and *b* being those actually there labelled :—

Face.	Circle Reading.	Interfacial Angle.
<i>b</i>	360° 0'	<i>bp'</i> = 30° 10'
<i>p'</i>	329 50	<i>p'p</i> = 29 57
<i>p</i>	299 53	<i>pa</i> = 29 52
* <i>a</i>	270 1	<i>ap</i> = 29 48
* <i>p</i>	240 13	<i>pp'</i> = 30 0
* <i>p'</i>	210 13	<i>p'b</i> = 30 12
* <i>b</i>	180 1	<i>bp'</i> = 30 14
<i>p'</i>	149 47	<i>p'p</i> = 29 58
<i>p</i>	119 49	<i>pa</i> = 29 49
<i>a</i>	90 0	<i>ap</i> = 29 47
<i>p</i>	60 13	<i>pp'</i> = 30 0
<i>p'</i>	30 13	<i>p'b</i> = 30 13
<i>b</i>	0 0	

From an inspection of this table of angles four most interesting and important facts are to be derived, namely :—

- (1) Twelve faces have been adjusted parallel to the goniometer axis

by the mere act of adjusting two of them. These twelve faces may be said to constitute a "zone." The direction of their edges of intersection, which are all parallel to the goniometer axis and to each other, will be the "zone axis"; and all the faces, their edges of intersection, and the zone axis are perpendicular to an imaginary plane which may be termed the "zone plane."

(2) The arrangement of the twelve faces in the zone is obviously a regular one, based on a definite plan of symmetry; that is to say, there is a regular repetition of similar faces at the same angular intervals.

(3) Every face has a parallel face on the other side of the crystal, at truly  $180^\circ$  from it, hence the imaginary centre of the crystal is a centre of symmetry.

(4) The two pairs of faces  $aa$  and  $bb$ , each pair consisting of two parallel faces, are arranged at right angles to each other, and the intermediate faces  $p$  and  $p'$  are distributed symmetrically on each side of them, that is to say, in such a regular manner that the planes  $a$  and  $b$  are planes of symmetry.

An analysis of the table of angles shows that the latter fall into three groups of equal angles, the maximum difference from equality of the individual values for the three groups being only  $4'$ ,  $3'$ , and  $5'$  respectively, limits within which the same angle on different crystals of the same substance and of fairly high perfection may vary, so that they can be equally well accepted as indicating intended equality in the case of symmetrical angles of the same zone on the same crystal. The three groups, together with their mean values, are given below. But it cannot be too prominently emphasised that the mean value must never under any circumstances whatever be taken until the question of the symmetry has been definitely settled from a consideration of the individual angular values themselves.

Angles between $b$ and $p'$ Faces.	Angles between $p'$ and $p$ Faces.	Angles between $p$ and $a$ Faces.
30° 10'	29° 57'	29° 52'
30 12	30 0	29 48
30 14	29 58	29 49
30 13	30 0	29 47
Mean value } 30° 12'	Mean value } 29° 59'	Mean value } 29° 49'
for $bp'$	for $p'p$	for $pa$

The symmetry will be at once apparent if these results are expressed graphically, as in Fig. 34, in which the positions of the intersections of the normals to the various faces with a circle of reference, which represents the goniometer circle, are indicated by circular dots.

The shading will render the symmetry clear, for the angles shaded with continuous lines are each  $30^\circ 12'$ , those shaded with dotted lines are  $29^\circ 49'$ , and those not shaded are  $29^\circ 59'$ . The fact that the planes  $aa$  and  $bb$  are planes of symmetry will also be quite obvious.



Before passing to the consideration of other faces on the crystal, it may be inquired, how do these mean values for the three angles on this crystal compare with similar results derived from other crystals of potassium sulphate? From eleven excellent crystals, yielding respectively 32, 30, and 29 different and independent values of  $bp'$ ,  $p'p$ , and  $pa$ , the final mean angles  $30^\circ 12'$ ,  $30^\circ 0'$ , and  $29^\circ 48'$  were obtained, and these are the values for these three angles which were published by the author. This closeness, the difference from the values for the crystal under consideration (one of the eleven) being *nil* in one case and only one minute in the other two, will afford some idea of the extraordinary precision with which nature achieves her aim when left undisturbed, and the truly wonderful degree of refinement to which the law of constancy and individuality of crystal angle is carried.

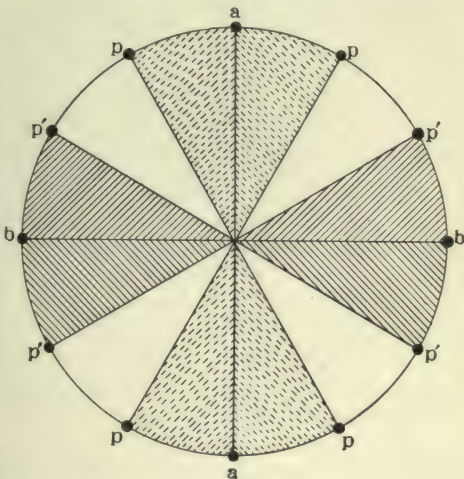


FIG. 34.

Another fact which is evident from the table of angles and Fig. 34 is that the symmetry is almost hexagonal, for the angles are all within a few minutes of  $30^\circ$ . It is not strictly hexagonal, however, for the difference of  $12'$  is well beyond the limits of possible error. For instance, among all the eleven crystals and thirty-two measurements of different  $bp'$  angles, the nearest value to  $30^\circ$  was  $30^\circ 8'$ , while the farthest from  $30^\circ$  was  $30^\circ 15'$ , the mean being  $30^\circ 12'$  as already given. Hence there can be no possible doubt that the crystal angle  $bp'$  is larger than  $30^\circ$ . It is in cases like this that a novice in crystal measurement might be inclined to jump to the conclusion that hexagonal symmetry was really intended, and might take the mean of the whole of the angles in the zone, which would then be bound to work out to exactly  $30^\circ 0'$ , a twelfth aliquot part of  $360^\circ$ . In so doing he would fall into the worst possible form of error. Such symmetry as we have here is called pseudo-hexagonal, but it is really of the type termed orthorhombic, which will subsequently be fully described in Chapter XIV. Before anything can be decided, however, as to the symmetry the other faces of the crystal must be studied, and attention will now be directed to them.

The crystal-holder should be removed from its position at the head of the adjusting movements, and the crystal reset on the wax cone in such a manner that it stands on an  $a$  face, with the faces  $b$  and  $c$  vertical. The holder should then be replaced in position and rotated until the

broad *b* face is approximately parallel to the tangent screw of one of the adjusting movements. The faces *b* and *c* are next to be adjusted

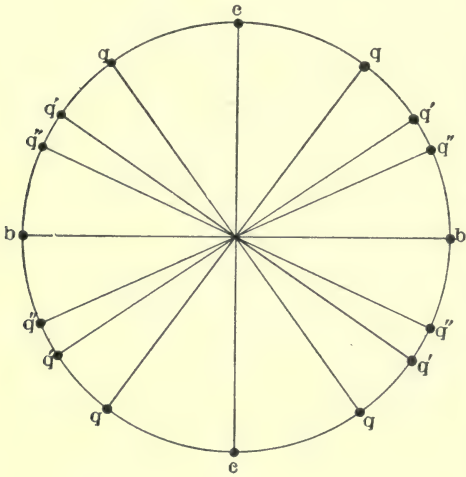


FIG. 35.

and centred exactly as in the former case of *a* and *b*. It will then be found that not only are these two faces and their two parallel faces adjusted, but also a whole series of intermediate faces, *q*, *q'*, and *q''*, repeated symmetrically in each quadrant, are equally accurately adjusted. In short, there is again presented the phenomenon of a "zone" of faces. Their disposition will be rendered clear by Fig. 35, and the actual values found for the various angles are given in the next table. Similar angles are collected together in the further short

tables, and, after being thoroughly satisfied that only such values are grouped together as are really symmetrically equivalent, their means taken. These latter values are very close to the mean values for the whole eleven crystals, which were respectively:  $bq' = 33^{\circ} 59'$ ,  $q'q = 19^{\circ} 26'$ ,  $qc = 36^{\circ} 36'$ ,  $q'q'' = 9^{\circ} 44'$ , and  $q''b = 24^{\circ} 13'$ . The concordance is again to one minute of arc, and in one case absolute.

Face.	Circle Reading.	Interfacial Angle.
<i>b</i>	360° 0' A	$bq' = 34^{\circ} 2'$
<i>q'</i>	325 58	$q'q = 19 20$
<i>q</i>	306 38 A	$qc = 36 36 A$
<i>c</i>	270 2 A	$cq = 36 37 A$
<i>q</i>	233 25 A	$qq' = 19 23$
<i>q'</i>	214 2	$q'b = 34 2$
<i>b</i>	180 0	$bq' = 33 52$
<i>q'</i>	146 8 A	$q'q = 19 26 A$
<i>q</i>	126 42 A	$qc = 36 38 A$
<i>c</i>	90 4 A	$cq = 36 35 A$
<i>q</i>	53 29 A	$qq' = 19 31$
<i>q'</i>	33 58	$q'q'' = 9 44$
<i>q''</i>	24 14	$q''b = 24 12$
<i>b</i>	0 2 A	

TABULATION OF SIMILAR ANGLES.

$bq'$ .	$q'q$ .	$qc$ .	$q'q''$ .	$q''b$ .
34° 2'	19° 20'	36° 36' A	9° 44'	24° 12'
34 2	19 23	36 37 A		
33 52	19 26 A	36 38 A		
33 56	19 31	36 35 A		
Mean 33° 58'	Mean 19° 25'	Mean 36° 37'		

It will be again clear from the measurement of this zone, and especially from the contemplation of the graphical representation in Fig. 35, that  $bb$  and  $cc$  are planes of symmetry, about which the intermediate faces  $q$  and  $q'$  are symmetrically arranged. The face  $q''$  was only found developed once on this crystal, but it was found twice on several other crystals of the eleven measured, and on one crystal three times repeated in the zone, so that there can be no doubt that, like  $q$  and  $q'$ , as well as  $p$  and  $p'$  on the zone already considered, it belongs to a set of four faces, symmetrically situated two on each side of the plane  $b$ . Such a set of similarly symmetrically situated faces is termed a "**form**." It is for this reason that the same symbolic letter is given to each of the four such faces, a letter being assigned to each form.

The forms on the two zones now measured are eight in number, namely: (1) the two faces  $a$ , (2) the two faces  $b$ , (3) the two faces  $c$ , (4) the four faces  $p$ , (5) the four faces  $p'$ , (6) the four faces  $q$ , (7) the four faces  $q'$ , and (8) the four faces  $q''$ .

A form consisting of two parallel faces only, such as  $a$ ,  $b$ , and  $c$ , is conveniently termed a "**pinakoid**," from  $\pi\acute{\iota}\nu\alpha\kappa\acute{\iota}\varsigma$ , "a slab."<sup>1</sup> Each of the forms  $p$ ,  $p'$ ,  $q$ ,  $q'$  and  $q''$  is of "prismatic" character, for the four faces of each make up, if considered alone, an open four-faced prism, in section a parallelogram, a rhombus, the axis of the prism being vertical (normal to the  $c$  faces) in the cases of  $p$  and  $p'$ , and front-to-back horizontal (normal to the  $a$  faces) in the cases of  $q$ ,  $q'$  and  $q''$ .

With respect to the character of the signal-images afforded by the faces of the two zones now measured on the crystal under consideration, those yielded by the faces of the first zone were all of the most excellent quality, being brilliant and single, with two exceptions in which they were fainter owing to the faces being very small (narrow); in the two cases in question, however, they were sharp and single, so that the relative faintness was no drawback. The faces of the second zone were not so uniformly excellent, only about half the images being brilliant and single. Hence the degree of closeness of the values for the similar angles is not so

<sup>1</sup> The mode of derivation of the word "**pinakoid**" will render it clear that the term refers to *two* parallel faces. It is therefore quite incorrect to refer to a single face as a pinakoid. A form which consists of only a single face is properly designated a "**pedion**," from  $\pi\epsilon\delta\acute{\iota}\omicron\nu$ , a plane.



high as in the case of the first zone, but it is yet good and the mean values are highly trustworthy, as is proved by their agreement with those for the whole eleven crystals. It is of considerable importance that some indicating mark should be placed against circle readings corresponding to perfect single images, and the author employs the letter A for this purpose, and also to indicate angular values obtained by taking the difference between two A readings. In the tables of readings and angles which follow, and for the zone just given, this has been done. All the images for the zone *ab* were of A quality.

The next move should be to determine the relative position of the two zones, by measurement of the angle between the faces *a* and *c*, and thus to ascertain definitely that they are at right angles, as indicated by a cursory inspection; and also at the same time to ascertain the presence or absence of intermediate faces in the zone *ac*. On adjusting *a* and *c*, the crystal being set up on the wax cone on the broad face *b*, it was found that the four angles *ac*, *ca*, *ac* and *ca* were respectively  $90^{\circ} 0'$ ,  $90^{\circ} 1'$ ,  $90^{\circ} 2'$ , and  $90^{\circ} 0'$ ; and there were no intermediate faces present. Evidently, therefore, the three "zone planes" of the three zones of faces now investigated are at right angles to each other (a "zone plane" being the plane at right angles to the faces of a zone), the axes of the zones being respectively the normals to the faces *c*, *a*, and *b*, themselves also at right angles to each other. These three faces are obviously of prime importance as regards the symmetry of the crystal. If they and their parallel fellows were alone present they would form a rectangular solid block, the edges of which would be parallel to the three normals.

We may therefore at once take a further step in theoretical crystallography by stating that the directions of these three principal normals, in cases like the present when the three planes are mutually perpendicular, are taken as the "axes" of the crystal, *c* being the vertical axis, *a* the axis passing from back to front towards the observer, and *b* the lateral axis. In the most general (triclinic) type of crystal the angles between these principal normals would not be  $90^{\circ}$ , in which case the three axes chosen would be parallel to the intersecting edges of the three principal facial planes, and would be mutually obliquely inclined. But in the case before us the axes are rectangular. These three rectangular axes *a*, *b*, *c* of potassium sulphate may be considered, equally with the general case of oblique axes, to intersect, by moving them parallel to themselves till they do, at the centre of the crystal, and we have next to consider how their relative lengths are determined. The data are already partially to our hand, in the measurements of the positions of the intermediate faces in the two zones *ab* and *bc*.

If a "form" had been discovered, consisting of well-developed faces, on each of those two zones inclined at exactly  $45^{\circ}$  to the rectangular faces, we should probably have been dealing with a cubic crystal of three equal rectangular axes. But we have seen that the intermediate faces are not arranged at  $45^{\circ}$ , but at angles nearly but not quite  $30^{\circ}$  in the case of the zone *ab*, and at  $36^{\circ}$  and  $34^{\circ}$  respectively in the case of the zone *bc*. The symmetry has already been foreshadowed as being that of the ortho-

rhombic system, of three rectangular but unequal axes, and these angles are quite in accordance with such a supposition. It will be necessary to choose one "form" in each of these two zones as the fundamental one, determining the lengths of the axes by its intersection with them, and this will be  $p$  in the zone  $ab$  and  $q$  in the zone  $bc$ , for reasons which will be fully entered into later, but chiefly because it is agreed by convention that of the two lateral axes  $b$  shall be the longer. Before we are quite in a position to make this choice, however, it is essential that we should study the other faces on the crystal.

It will be obvious that the faces marked  $o$  in Fig. 32 are important ones, and that the smaller faces of similar octahedral or pyramidal character,  $o'$  and  $o''$ , are apparently arranged in the same zone with them, which zone also includes the  $c$  and  $p$  faces. This zone, moreover, occurs in duplicate, there being one such zone on each side of the plane of the axes  $a$  and  $c$ . The crystal was left in position on the goniometer with the zone  $ac$  adjusted, and it should now be tilted by the adjusting movement the tangent screw of which is parallel to  $c$  so as to bring one pair of faces  $p$  into adjustment with the pair of  $c$  faces. After completing the adjustment with the aid of the other tangent screw it will be found that the faces  $o$ ,  $o'$ , and  $o''$  are, as appeared likely, situated truly in the  $cp$  zone, and are consequently in perfect adjustment also. The zone should then be measured, and when this is completed the same tangent screw as before should be employed (working the segment over to the other side of the centre) to bring the other pair of  $p$  faces into adjustment with the  $c$  faces, so as to measure the duplicate zone  $cp$ . When the adjustment is complete, with the aid of the final touches from both tangent screws as usual, and the crystal properly centred, the  $o$ ,  $o'$ , and  $o''$  faces of this zone will also be found to be in perfect adjustment, and the zone can at once be measured. The measurements obtained with both the zones are set out side by side in the next table.

It will be immediately obvious that the angles of the right zone are equal to those of the left zone, and that, therefore, the plane between them, that of the axes  $a$  and  $c$ , is a plane of symmetry with respect to these zones, just as truly as it was found to be as regards the  $p$  and  $p'$  faces of the  $ab$  zone and the  $q$  and  $q'$  faces of the  $bc$  zone. The same is equally true of the relations of these two zones, and the individual angles of which they are made up, to the other two principal planes of the axes,  $ab$  and  $bc$ . So that these three axial planes, parallel to the faces  $a$ ,  $b$ , and  $c$  respectively, are undoubtedly planes of symmetry with respect to all the faces developed on the crystal, the inclinations of those faces being the same on either side of them.

It will be further observed that the faces  $o$  and  $o'$  are repeated eight times on the crystal, four on the right-hand zone and four on the similar zone to the left of the fundamental plane of the normals to  $a$  and  $c$ . The form  $o''$  was only represented by a single measurable face, but traces of several of the other seven possible faces were observed, the signal-images derived from them being, however, too faint for accurate allocation to the cross-wires. Each of these forms  $o$ ,  $o'$ , and  $o''$  is of "pyramidal"

Zone to right of <i>a</i> .			Zone to left of <i>a</i> .		
Face.	Circle Reading.	Interfacial Angle.	Face.	Circle Reading.	Interfacial Angle.
<i>c</i>	360° 0'A	<i>co'</i> 36° 42'A	<i>c</i>	360° 0'A	<i>co'</i> 36° 45'A
<i>o'</i>	323 18 A	<i>o'o</i> 19 30 A	<i>o'</i>	323 15 A	<i>o'o</i> 19 32 A
<i>o</i>	303 48 A	<i>op</i> 33 47 A	<i>o</i>	303 43 A	<i>op</i> 33 43 A
<i>p</i>	270 1 A	<i>po</i> 33 48 A	<i>p</i>	270 0 A	<i>po</i> 33 47 A
<i>o</i>	236 13 A	<i>oo'</i> 19 26 A	<i>o</i>	236 13 A	<i>oo'</i> 19 31 A
<i>o'</i>	216 47 A	<i>o'c</i> 36 47	<i>o'</i>	216 42 A	<i>o'c</i> 36 42
<i>c</i>	180 0	<i>co'</i> 36 44	<i>c</i>	180 0	<i>co'</i> 36 46
<i>o'</i>	143 16	<i>o'o</i> 19 25	<i>o'</i>	143 14 A	<i>o'o</i> 19 25
<i>o</i>	123 51 A	<i>op</i> 33 49 A	<i>o</i>	123 49	<i>oo''</i> 9 49
<i>p</i>	90 2 A	<i>po</i> 33 46 A	<i>o''</i>	114 0	<i>o''p</i> 24 0
<i>o</i>	56 16 A	<i>oo'</i> 19 28 A	<i>p</i>	90 0 A	<i>po</i> 33 51 A
<i>o'</i>	36 48 A	<i>o'c</i> 36 46 A	<i>o</i>	56 9 A	<i>oo'</i> 19 18
<i>c</i>	0 2 A		<i>o'</i>	36 51	<i>o'c</i> 36 50
			<i>c</i>	0 1 A	

Values of <i>co'</i> .	Values of <i>o'o</i> .	Values of <i>op</i> .	Values of <i>co'</i> .	Values of <i>o'o</i> .	Values of <i>op</i> .
36° 42'A	19° 30'A	33° 47'A	36° 45'A	19° 32'A	33° 43'A
47	26 A	48 A	42	31 A	47 A
44	25	49 A	46	25	49
46 A	28 A	46 A	50	18	51 A
36° 45'	19° 27'	33° 48'	36° 46'	19° 27'	33° 47'

character, for each of them, if alone present, would build up a doubly terminated pyramid, that is, two four-faced pyramids base to base.

**Stereographic Projection.**—We have now arrived at a stage in the measurement of the crystal of potassium sulphate when the need for a mode of graphically representing the whole of the faces of the crystal in a single drawing, showing at a glance the mutual arrangement of the various zones, is irresistibly borne in upon us. We have hitherto represented the zones separately, in Figs. 34 and 35, but these figures, while showing the symmetry of the faces in the one zone represented in each case, give no indication of the relationship of the zone drawn to any other zone. By thus discovering the want of such a condensed and complete graphical representation of the symmetry of the crystal for ourselves, we can at once appreciate the immense service which the stereographic projection, first introduced by Neumann in the year 1823, has been to crystallography.

The essence of the method of the stereographic projection is that the normals to the crystal faces are considered as the radii of a sphere. It is hence sometimes called the "spherical projection," although strictly speaking this term applies to the actual projection on the surface of a sphere, while "stereographic projection" refers to the projection of the latter on to the plane of the paper, as actually used. It was clearly shown in Chapter I. that the relative amount of development of crystal faces is quite a secondary matter, without influence on the symmetry, and



that the direction of the faces, as indicated by their mutual inclinations, is what is of real moment in determining the symmetry and in offering, by the constancy of the angles, an infallible guide to the individuality of the crystallised substance. Our stereographic projection, therefore, takes cognisance only of the directions of the faces, as represented most conveniently by their normals.

An arbitrary point within the crystal is taken as the centre of the sphere of projection, or origin, and radii are drawn from it perpendicular to the crystal faces, or to their planes produced. Each of these radii will meet the sphere in a point which is termed a "pole," and from the disposition of these poles, which are taken as representing the faces, the symmetry of the crystal can be seen at a glance. It requires to be clearly understood at the outset, however, that the normal drawn from the centre will not necessarily pass actually through the face itself, because it may happen that the face is very small and thrown out of the line of the normal to the indefinitely produced and extended face, owing to the specially large development of other faces; the faces are, however, considered as planes of indefinite extent, to which the normals are drawn perpendicular from the centre. The spherical projection thus gets rid of the confusion due to the fortuitous development of particular faces, and presents a graphical expression of the arrangement of the faces, indicative immediately of the symmetry, and showing the facial poles at their correct angular distances, as determined directly by the measurements. For, as has been clearly shown already, it is the angles between the normals which are directly determined on the goniometer.

In order to render this most important conception absolutely clear, we may imagine the crystal, exhibiting the ideal even development of faces so rarely attained in actual fact, to be placed in the middle of a sphere of jelly, as indicated in Fig. 36 (which is due to the late Prof. Penfield), so that the centre or origin of the axial system and the centre of the sphere coincide. It is then to be further imagined that long needles are stuck through the jelly and the crystal, one perpendicular to each crystal face and so as to reach the centre. The crystal represented in the figure is a combination of the cube *a*, octahedron *o*, and rhombic dodecahedron *d*. The needles would then emerge at the surface of the sphere in points (poles) which would lie on great circles (circles representing the intersection of the sphere by planes passing through the centre). The points would be distributed along these great circles at regularly recurring

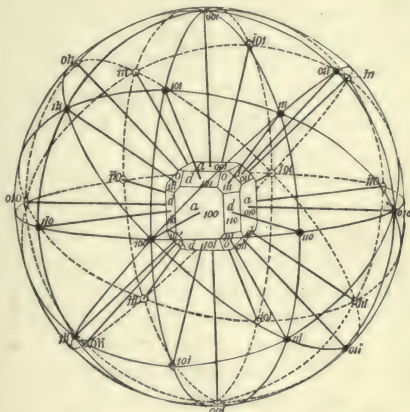


FIG. 36.—The Spherical Projection.

positions, corresponding to the symmetry of the crystal. If, as in the case shown, the crystal belonged to one of the higher systems of symmetry (here the cubic), it would happen that four of the points on at least one of these great circles, and possibly on three of them as in the case drawn in the figure, would be exactly  $90^\circ$  apart, at the ends of rectangular diameters, and these latter would most likely (as here is the case) be the crystallographic axes of reference. The other points would be distributed symmetrically on each side of these four points. The great circles would be zone-circles, and tangents to them at the points would be parallel to the faces, which would be those of a zone. In order to convert this spherical projection on the surface of the jelly sphere into the invaluable "stereographic projection," we have only to imagine the sphere to be projected on to the flat surface of a sheet of drawing paper, on the supposition that the eye is placed at either the north or south pole of the sphere, and that the plane of projection is that of the equatorial great circle.

For in order to render the spherical projection really useful as a plan of the crystal faces, the sphere and its facial poles must obviously be projected on to a plane surface, the plane of the paper, and, in order to attain facility of construction, in such a manner that the poles of faces of the same zone will be represented in the projection as lying either on the same circular arc or on the same straight line. This is attained in the stereographic projection, for all the zone circles, formed by the intersection of the various zone planes with the sphere, are projected as circles and not as ellipses, which would be much more troublesome to construct. Their two limiting cases are: (1) the equatorial plane itself, the plane of projection, which is represented by a complete circle, termed the "primitive circle," and within the circumference of which the whole figure falls; and (2) those zone circles the planes of which are perpendicular to the primitive zone circle, which project into straight lines (diameters of the primitive circle) intersecting at the centre of the primitive circle and of the sphere which it represents in plan. The centre is also the projection of the "pole of projection," which lies on the surface of the sphere. The actual mode of constructing the "stereographic projection" will now be described.

The zone plane of one of the most prominent zones of faces on the crystal is chosen as the plane of projection. This plane is supposed to pass through the centre of the sphere, and the axis of the zone is of course perpendicular to it and is supposed to be projected in the point which forms the centre. The sphere will be cut by the plane in a circle, the primitive circle, and a circle is consequently described round the centre, of convenient radius, to represent this primitive circle. The sphere is thus divided by this circle into two hemispheres, and each hemisphere is projected upon the plane of projection by imagining the eye placed at the geometrical pole<sup>1</sup> of the other hemisphere. For there are really two poles of projection, one for each hemisphere, and each is naturally

<sup>1</sup> It is very essential to distinguish clearly between (a) the two geometrical poles (north and south) of the sphere—the poles of projection—and (b) the facial poles. The former are themselves also facial poles when a pair of faces are present on the crystal parallel to the plane of projection, as is very often the case with all but triclinic crystals.



removed  $90^\circ$  from every point on the primitive circle. Both obviously have, therefore, the centre of the primitive circle for their projection point. If straight lines be drawn from this pole of the one hemisphere to all the poles of faces (the points where the face-normals cut the sphere) on the other hemisphere, these straight lines will cut the plane of the primitive circle (the plane of projection) in points which are the required projections of those face-poles. The same plane of projection can also be used on which to project, from the eye situated at the pole of the other (opposite) hemisphere, the poles of faces in the second hemisphere, in exactly the same manner. If the plane of projection be a plane of symmetry, as is true in the cases of all but triclinic crystals, the projection points of the facial poles of the two hemispheres will coincide on the plane of projection, and such pairs of poles are usually represented by a dot with a miniature ring around it (the ring, however, is often omitted). They may be regarded as joined by imaginary straight lines perpendicular to the plane of projection, and of equal lengths above and below it.

**Construction of Stereographic Projection for Typical Crystal of Potassium Sulphate.**—We will now proceed to construct the stereographic projection of potassium sulphate, and in so doing the main rules for the construction of such projections in general will be elucidated.

The directions of the edges of intersection of the faces  $a$ ,  $b$ , and  $c$  have already been chosen as the crystallographic axes, and as the three faces are all perpendicular to each other, these directions are obviously identical with those of the normals to the three faces. It has also been decided that  $a$  shall run between back and front, that  $b$  shall be the lateral axis (running right and left), and that  $c$  shall be the vertical axis. We take, therefore, the zone plane of the zone of faces  $app'b$  as the plane of projection, and describe our primitive circle, Fig. 37, with any convenient centre and radius, to represent it. We also draw the axial diameters  $aca$  and  $beb$  at right angles to each other. The correct positions of the intermediate faces  $p$  and  $p'$  are then to be set off, as was already done for Fig. 34, in accordance with the measurements, and these positions must be indicated by circular dots to represent the poles, two pairs of similar dots being also placed at the positions of the fundamental faces  $a$  and  $b$ . The centre is the pole of the

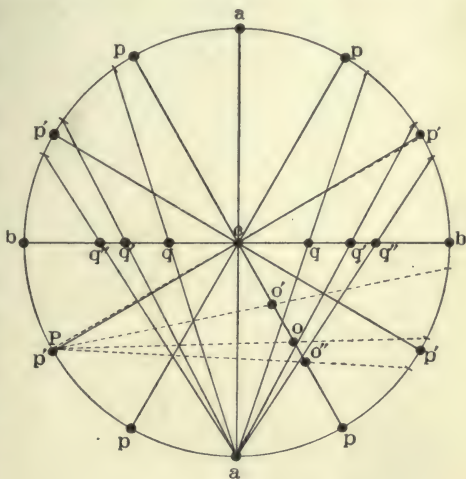


FIG. 37.



pair of  $c$  faces, and should, therefore, also be marked with a dot. Opposite pairs of parallel faces should then be joined by diameters, and as all these diameters will naturally pass through the centre  $c$ , they will be the projections of possible zones, of which  $c$  will furnish a pair of faces.

No faces were observed between the  $a$  and  $c$  faces in the zone  $ac$ , but in the zone  $cb$  there were three forms of intermediate faces found, namely,  $q$ ,  $q'$ , and  $q''$ , and their positions are next to be found on the projection. In order to achieve this it is only necessary to set off from  $b$  along the primitive circle arcs equal to  $bq''$ ,  $bq'$ , and  $bq$ , and to join these points on the circle to the pole (in the opposite hemisphere) of the zone circle (projected as diameter)  $bc$ , this pole being the point  $a$ . The points in which these straight lines will cut the diameter  $bc$ , representing the zone circle, will be the projections of the required poles of the faces  $q$ ,  $q'$ , and  $q''$ . This should be done for the three such poles on each side of the centre, as shown in Fig. 37, in which the lower  $a$  pole is taken as the pole of the zone  $[bc]$ , the markings off of the angles  $bq$ ,  $bq'$ , and  $bq''$  having been carried out along the upper semicircle.

The positions of the poles of the faces  $o$ ,  $o'$ , and  $o''$  in the two similar zones  $cp$  may next be found in the same way. For the projections of these zones are the diameters  $pcp$ . It is necessary first to mark off the position of one of the poles of these zones, say  $P$ , at  $90^\circ$  from  $p$  on the primitive circle; then to set off along the primitive circle from  $p$ , on its other side away from  $P$ , the angles  $po$ ,  $po'$ , and  $po''$  corresponding to the intermediate faces  $o$ ,  $o'$ , and  $o''$ , and to join these points to the pole  $P$  just found, as shown in Fig. 37 in dotted lines. Where they intersect the radius  $cp$  are the positions of the facial poles  $o$ ,  $o'$ , and  $o''$ . This only need be done on one side of  $c$ , for the angles are the same on the other side and can be simply pricked off at the like distances by the compasses. The poles of the similar zone  $cp$ , on the other side of the plane of symmetry of which the diameter  $aca$  is the projection, can also be marked off with the compasses at the same time, and in this manner all the eight poles of the forms  $o$ ,  $o'$ , and  $o''$  may be found, and the positions of all the forms observed on the crystal will then have been located. The stereographic projection thus completed, and to which Figs. 34, 35, and 37 have led up, is shown in Fig. 38. The poles of three other forms,  $q''' = \{012\}$ ,  $m = \{102\}$ , and  $s = \{132\}$ , are included on it, as these forms have been discovered by the author on other isomorphous salts of the alkaline sulphate and selenate series. It will be remembered that the poles  $o$ ,  $o'$ ,  $o''$ ,  $q$ ,  $q'$  and  $q''$  each represent two faces, one in the hemisphere above the plane of projection and one in the hemisphere below. The dots may therefore each be ringed to mark this fact (as shown in the example in Fig. 135), although in general practice the fact is taken as understood, and the rings omitted.

On studying the projection thus obtained, a further interesting fact is apparent, namely, that the zones indicated by the primitive circle itself, and the six diameters, representing great circles the planes of which are perpendicular to the primitive circle and plane of projection, are not the only zones into which the faces fall, but that they also arrange them-

selves into eight other zones, along which the angles ought to be measured. If circular arcs, for instance, be drawn through the points *a* and *o*, to either the right or left, the arc will be found in both cases to pass also through the pole *q*; and if arcs be also drawn through the poles *p* and *o'* of adjacent quadrants they will be similarly found in both cases to pass also through *q*. In Fig. 38 arcs have been drawn to connect the poles of all the chief zones, thus finally completing the stereographic projection of the example chosen, potassium sulphate. This mode of projection is thus exceedingly valuable from another point of view, namely, that when the few main zones have been discovered experimentally and drawn into the projection, the latter at once shows that the faces are also arranged along other zones, and so suggests the course of the further measurements, which should be carried out along those additional

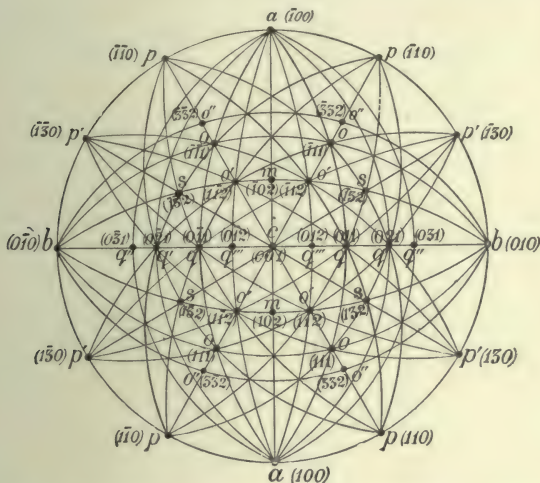


FIG. 38.—Stereographic Projection of Alkali Sulphates and Selenates.

zones. In the next tables are given the measurements along eight such further zones in the case of the crystal before us, namely, those along which the circular arcs are drawn.

The two pairs of zones  $aoq$  and  $ao'o'$  are most conveniently measured by setting the crystal on the wax and arranging the holder as if the zone  $ac$  were to be again adjusted and measured; then leaving the  $a$  faces so adjusted but rotating the other tangent screw so as to bring first the  $q$  face on one side of  $c$  into adjustment instead of  $c$ , and after measuring that zone, then the  $q$  face on the other side of  $c$ . Similarly, with the same setting, the two zones comprised by the  $a$  and  $o'$  faces may be adjusted and measured. In the case of the pair of zones  $bo$  and  $bo'$  the crystal should be set again as if to measure the zone  $ab$ , and then, while keeping the  $b$  face as adjusted, the crystal should be rotated with the other tangent screw, on each side of  $a$  in turn, so as to bring also into adjustment the

desired  $o$  or  $o'$  face, parallel to the goniometer axis. In order to measure the four pairs of zones  $poq'$ ,  $po'q$ ,  $p'oo'q'$ , and  $p'o'q$ , it is necessary to be able to recognise the various faces at sight, and as these more difficult zones are left to the last, by this time the observer will have become thoroughly familiar with the peculiarities of the faces, and can readily recognise any particular face. If any difficulty should, however, be experienced in doing so, it is a great help if, while measuring the earlier fundamental zones, little rough sketches of the shapes or marking of the different faces have been made. An example is given in Chapter XI. (first zone of cobaltite). When thus at home among the various faces no difficulty will be experienced in adjusting any, even the most complicated, zone to the required position for measurement, namely, with its zone axis parallel to the goniometer axis. The tables referred to, of the results of the measurements of these zones, now follow :

Zone $aoq$ .	Zone $bo$ .	Zone $poq'$ .	Zone $p'oo'$ .
$ao = 43^\circ 52'$ $oq = 46 \quad 8$	$bo = 65^\circ 36'$ $oo = 48 \quad 47$	$po = 65^\circ 9'$ $oq' = 49 \quad 11$ $q'p = 65 \quad 40$	$p'o = 43^\circ 59'$ $oo' = 45 \quad 47$ $o'q' = 46 \quad 0$ $q'p' = 44 \quad 13$
Zone $ao'$ .	Zone $bo'$ .	Zone $po'q$ .	Zone $p'o'q$ .
$ao' = 58^\circ 44'$ $o'o' = 62 \quad 34$	$bo' = 72^\circ 42'$ $o'o' = 34 \quad 36$	$po' = 72^\circ 23'$ $o'q = 34 \quad 52$ $qp = 72 \quad 46$	$p'o' = 58^\circ 48'$ $o'q = 62 \quad 14$ $qp' = 58 \quad 58$

The actual circle readings are not recorded here, as the method of arranging them in the note-book has been sufficiently indicated in connection with the earlier zones. It will be enough to state that in passing round the complete zone  $aoq$ , the angles  $ao$  and  $oq$  are each met with four times, and as there are two such zones the crystal furnishes these angles eight times each, and the values given in the above table are the mean of the eight in each case. Similarly,  $ao'$  occurs eight times, and  $o'o'$  four times;  $bo$  and  $bo'$  each occur eight times and  $oo$  and  $o'o'$  four times, and the mean values are given in the table. In the cases of the remaining four cross zones, each angle is repeated (occurs in duplicate) in each zone, and as each zone is itself repeated (the pair of zone circles being symmetrical to the diametral plane  $pc$  or  $p'c$ , although the poles themselves are only arranged on them symmetrically to the centre), four values are afforded in all for each angle, and the mean of the four is given in the table.

Having now completed the measurements of the interfacial angles of the typical crystal of potassium sulphate, it will be well to take stock of the facts which have been learnt during the process. The mode of utilising the measurements for the calculation of the elements of the crystal, and the checking of the measurements by calculation, will be dealt with in Chapter VIII., after the essential principles have been elucidated on which descriptive crystallography is based, and to which this chapter has afforded an introduction.



**Summary of Facts revealed by Measurement of a Typical Crystal.—**

(1) Each face developed on the crystal has been found to be accompanied by a parallel face on the opposite side of the crystal, so that the centre of the crystal is a "centre of symmetry."

(2) The faces have been found to lie in "zones," which are such that when any two faces, other than a parallel pair, have been adjusted parallel to the axis of the goniometer, the whole of the remaining faces of the zone to which these two belong are also found to be equally accurately adjusted parallel to the goniometer axis, so that by rotation of the latter the signal images reflected from all the faces in turn are brought into the field of view and in perfect adjustment symmetrical to the horizontal spider-line.

(3) The faces of any and every zone have been found to occur in a regular order of repetition, dependent on a definite plan of symmetry according to which the whole scheme of faces is arranged.

(4) The crystal exhibits three pairs of fundamentally important faces,  $a$ ,  $b$ , and  $c$ , inclined at exactly  $90^\circ$  to each other, and all the other faces, as also their zones, are arranged symmetrically as regards their inclination to these three planes, which may thus be termed "planes of symmetry." Their intersections may be taken as the three rectangular "axes" of the crystal.

(5) The faces not only fall naturally into zones, but into sets (each set consisting of different faces) of two, four, or eight similarly orientated faces with respect to the symmetry, which are termed "forms." The faces  $a$ ,  $b$ , and  $c$  occur in pairs, termed "pinakoids"; the faces  $p$ ,  $p'$ ,  $q$ ,  $q'$ , and  $q''$  occur in fours, and are of "prismatic" character; and the faces  $o$  and  $o'$  occur in eights, and are of double "pyramidal" character, consisting of two four-faced pyramids base to base.

(6) The "stereographic projection" represents the arrangement of the faces of a crystal in a highly convenient manner, the confusion due to fortuitously large or small relative development of particular faces being eliminated, while the order of symmetry is prominently displayed. It has the further great convenience that the interfacial angles directly read off on the goniometer, the angles between the normals to the faces, are those actually graphically expressed in the projection, which is that of an imaginary sphere enveloping the crystal, projected on to the plane of the paper, the circular dots or "poles" representing the crystal faces being the projections of the points of intersection of the face-normals with the sphere. The projection shows all the zones either as circular arcs (a complete circle in the case of the primitive circle representing the plane of projection) or diametral straight lines, so that it can be readily constructed with the aid of a pair of compasses and a ruler. It is a most valuable aid in discovering the more complicated cross-zones, other than the fundamental ones; and, moreover, it lends itself immediately to the methods of calculation of spherical trigonometry.

## CHAPTER V

### CRYSTAL AXES, INDICES OF FACES, AND LAW OF RATIONALITY

**Crystal Axes.**—It was shown in Chapter IV. that three important faces, parallel to planes of symmetry if the crystal be endowed with such, are chosen as the axial planes, and their intersections as the fundamental crystal “axes,” to which for descriptive purposes the whole morphology of the crystal is referred. If, as was the case with the typical crystal of potassium sulphate studied in that chapter, there were three planes inclined at  $90^\circ$  to each other developed on the crystal, these planes would naturally be chosen as the axial planes, and the axes of the crystal would then be mutually perpendicular to each other. In the stereographic projection (Fig. 38) these three axes are represented by the diameters *aa* (running back and front) and *bb* (running right and left), and by the central point *c*, which represents in plan the third axis perpendicular to the plane of projection. As will be shown in detail in subsequent chapters, in considering the various possible types of crystal symmetry, the three axes are by no means necessarily at right angles to each other, and it is best to consider the general case, which does actually occasionally occur in the crystals of a few substances, namely that of the so-called triclinic crystals, in which the three axes are inclined to each other at unequal angles and are of unequal lengths. In Fig. 39 *XOX'*, *YOY'*, *ZOZ'* represent the three crystal axes intersecting at a centre *O*, and the directions of which are parallel to the intersections of three principal faces of the crystal, *ABO*, *ACO*, *BCO*. Each of these three facial planes may be and generally is represented on the crystal by two parallel faces at opposite sides of the crystal, that is, on opposite sides of the centre *O*, as shown in Fig. 40, where the faces *a*, *b*, and *c* each have a parallel fellow indicated by dotted lines, as they would be invisible if the crystal were opaque. The actual edges of intersection formed by these three pairs of faces on the crystal are twelve in number, consisting of three sets of four parallel and equal edges. The three different edges meeting in any one of the eight corners of the solid are those which are taken as the directions of the three axes, and they can be imagined without any impropriety to be moved parallel to themselves so as to bring the corner to the centre *O* of the crystal, when they will correspond to *OX*, *OY*, and *OZ* of Fig. 39. Each of the three axes will then radiate from *O* through the middle of a

parallel pair of faces, as shown in Fig. 40,  $A, A', B, B', C,$  and  $C'$  being the six points of emergence. For the amount of development of the crystal in any direction is a purely fortuitous circumstance, and, as has been amply proved, is without influence on the angles of mutual inclination of the faces, which angles are the real expression of the crystal structure. The planes  $XOY, YOZ,$  and  $XOZ$  are termed the "axial planes," and the angles between the axes, which are the same as the angles between the crystal edges, are termed the "axial angles," and are labelled  $\alpha, \beta, \gamma,$  in the order shown in Fig. 39. These angles are not to be confounded with those between the crystal faces chosen as axial planes, with which they are only identical when at least one plane of symmetry is developed, as in crystals belonging to the system termed monoclinic; in triclinic crystals they are never identical. The axes themselves are generally labelled  $a, b, c,$  and the angle  $\alpha$  is opposite to the axis  $a$ , the angle  $\beta$  is opposite to the axis  $b$ , and the angle  $\gamma$  is opposite to the axis  $c$ . The three fundamental faces themselves are also generally labelled  $a, b,$  and  $c$ , as well as their parallel fellows, according to the axis which emerges through

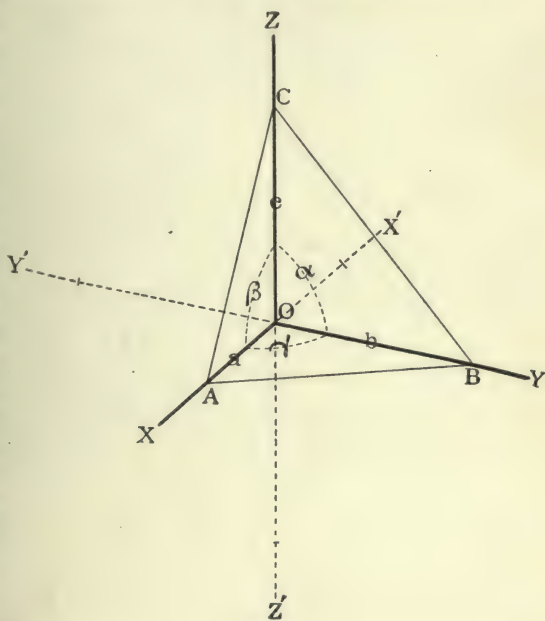


FIG. 39.

them (except when the crystal is cubic and all six are then faces of the same form, the cube, and are lettered  $a$ ; or tetragonal, when both  $a$ - and  $b$ -faces are one form and lettered  $a$ ). Hence the interfacial edge  $cb$  is parallel to axis  $a$ , the edge  $ac$  to axis  $b$ , and the edge  $ab$  to axis  $c$ , in each case the edge being parallel to that axis the letter expressing which does not occur in the two letters representing the faces intersecting in the edge. This will be quite clear from Fig. 40. The three planes containing the axes divide up the space within the crystal into eight parts, which are referred to as "octants."

When a fourth face  $ABC$  (Fig. 39) inclined to all three axes is present on the crystal, such as the face  $o$  in Fig. 40, in addition to the three fundamental faces (and their parallel fellows) chosen as the directions of the axial planes, it will cut the axes in lengths  $OA, OB, OC$ , which are termed



the "parameters" of the face. These parametral axial lengths cut off by a selected fourth face serve the purpose of defining the position not only of the fourth face in question, but also, by making use of them as standard or unit lengths, that of any other face on the crystal, with respect to the three axes, just as in solid geometry any plane is defined by reference to three axes in space. In the case of the fourth or parametral plane itself the ratio of the three parametral lengths at once gives the position of the face, whereas for all other faces inclined to all three axes the lengths are expressed relatively to these fundamental lengths. In order that the definition of the position of a face may be complete,

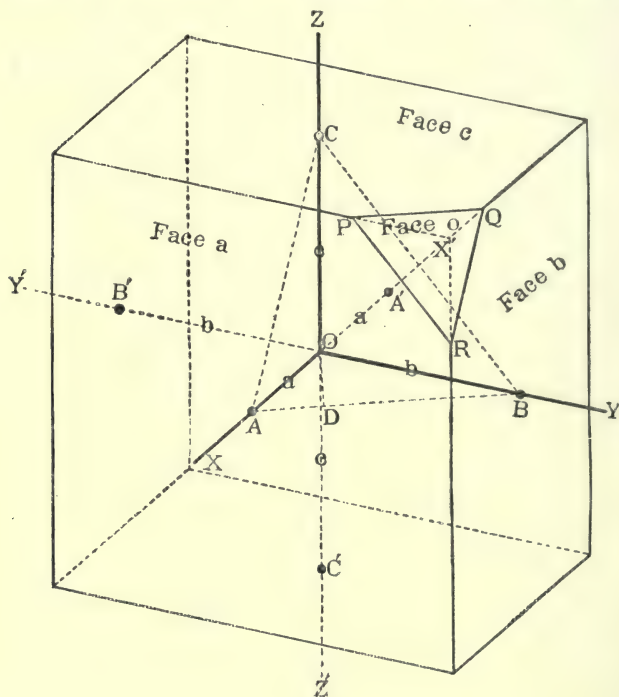


FIG. 40.

however, it is necessary to know also the particular octant in which the face produces, by its intersection with the axes, the triangle corresponding to ABC; this closed figure formed by the plane ABC and the axial planes then defines the position, even although the face spreads over into other octants after intersection with the axes. As there are eight octants, there will be eight faces possible having similar parameters, the whole making up an octahedral solid having the shape of two four-faced pyramids base to base; and to distinguish the octant referred to by any particular set of parameters, intercepts falling in the back and left-hand halves OX' and OY' of the lateral axes XOX' and YOY', and on the lower half OZ' of the vertical axis ZOZ', are marked with the negative sign -.

It will be obvious that the parameters of any face may be multiplied or divided by any number whatsoever without altering their ratio, and it is the last alone which determines the angular position of the face; mere extent of development has been shown to be of no moment whatever as regards defining the elements of the crystal structure, merely resulting in certain faces being pushed outwards parallel to themselves and certain others withdrawn parallel to themselves. Consequently, it is quite permissible to represent the parameters by the simplest numbers which will exhibit their ratio correctly, and it is therefore customary to express the primary parameters, those of the selected fourth face, so that one parameter = 1, the right and left lateral axis  $b$  being now universally chosen as this axis of unit length.

If, therefore, we choose the face ABC as representing the "primary" or "unit" form,—because it cuts all three axes at lengths not far removed from equality, or by reason of its prominent development, or because cleavage is developed parallel to it,—its parameters  $OA = a$ ,  $OB = b$ ,  $OC = c$  will be the "**lengths of the axes**," and their ratios  $a : b$  and  $c : b$  (as  $b = 1$ ) will be the "**axial ratios**" of the crystal. When referring to the crystallographic axes it is customary to restrict the use of the three small letters  $a$ ,  $b$ ,  $c$  to the designation of these relative parametral lengths of the three axes  $OA$ ,  $OB$ ,  $OC$ , and, as already mentioned, to make  $b = 1$ . Thus  $a$ ,  $b$ ,  $c$  do not only signify the axial directions, but definite relative lengths along those directions. The ratios thus generally (now practically universally) take the form  $a : b : c$ , that is,  $a : 1 : c$ . As the axis  $b$  is generally chosen as the longer horizontal axis the value of  $a$  will be less than unity. The value of  $c$  is in general something between 0.5 and 1.5. The actual figures are expressed in each case to four decimal places. For instance, in the case of triclinic copper sulphate, it will be shown in Chapter XIX. that  $a : b : c = 0.5715 : 1 : 0.5575$ .

**Elements of a Crystal.**—The two ratios  $\frac{a}{b}$  and  $\frac{c}{b}$ , together with the three interaxial angles  $\alpha$ ,  $\beta$ ,  $\gamma$ , are termed the "**elements**" of the crystal, and the four primary planes which determine the elements, namely, the three axial planes and the primary parametral plane inclined to them, are termed the "**elementary faces**" of the crystal.

In the case of highest symmetry, which will subsequently be shown to be found in the cubic system, the three axes are of equal lengths and are arranged at right angles to each other; moreover, their planes are planes of symmetry. In this case the ratio of the axes, as determined by the primary inclined form, the regular octahedron, will simplify to  $1 : 1 : 1$ , and the interaxial angles are each  $90^\circ$ . Between this case of perfect symmetry and the general case of triclinic crystals, in which the three axes are of unequal lengths and are all inclined at angles other than  $90^\circ$  to each other, and in which also the crystal is without any planes of symmetry, it will be shown in subsequent chapters that there are several stages of intermediate symmetry. In the case of the orthorhombic potassium sulphate crystal investigated in the last chapter, the axes are arranged rectangularly, so that all the interaxial angles are  $90^\circ$ ,

but the three axes are of unequal lengths ; their three planes are, however, planes of symmetry. The actual ratio of the axes found was  $a : b : c = 0.5727 : 1 : 0.7418$ , and the mode of calculating it will be dealt with in Chapter VIII.

**Indices of a Face.**—Having decided which faces to choose as the four elementary faces and consequently settled the “elements” of the crystal, any other face  $HKL$ , Fig. 41, can at once be defined as regards its position and direction by the “intercepts” which it makes, or lengths (relative

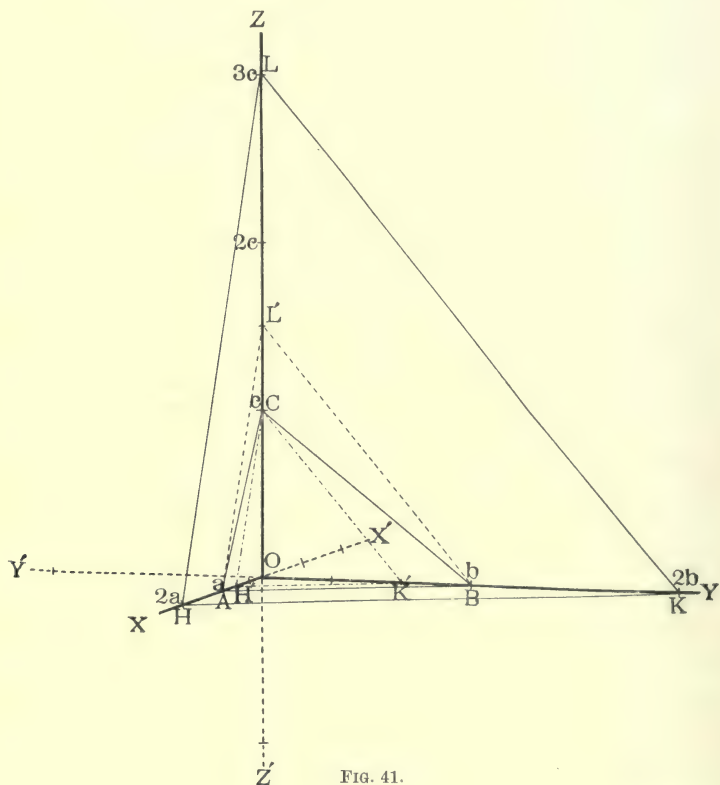


FIG. 41.

to the axial lengths  $a, b, c$ ) which by its intersection it cuts off, along the three axes. We can express those intercepts in terms of the axial lengths, the primary intercepts or parameters,  $a, b, c$ , by stating them as  $ma : nb : rc$ . For instance, the face  $o''$  on the potassium sulphate crystal dealt with in the last chapter—and which, as well as the rectangular axes  $a, b, c$  and the parametral face  $ABC$ , is drawn as  $HKL$  in Fig. 41 correctly to scale according to the customary convention to be described in Chapter XXV.—makes the intercepts on the three respective axes :  $2a : 2b : 3c$ ; this expression, therefore, may be taken as the symbol of the face. This is



the **Weiss notation**, or method of distinguishing crystal faces, having been proposed by Weiss in the year 1818.

According to the simplest form of this notation, in the case of a face having different intercepts on the three axes, the longer ones are expressed as multiples of the shortest, which latter is taken as unity. For instance, in the case just quoted the relationship is equally expressed by the symbol  $a : b : \frac{3}{2}c$ , and the dotted lines ABL' indicate the position of the face in Fig. 41, just as well as the parallel plane HKL. The faces other than the primary are thus considered as lying outside the latter, but in contact at one point or along a line. In this case there is contact along the line AB, which would thus be the direction of intersection of the primary parametral face and the face in question.

To take another example, suppose the intercept on the axis  $a$  to be the same as that of the primary form, that on  $b$  being  $1\frac{1}{2}$  times that of the primary form and that on  $c$  3 times the primary value; the symbol will then be  $a : \frac{3}{2}b : 3c$ . Here there is contact at the point  $a$  only with the primary plane.

For the parallel face in the lower, back, left octant, all the signs would be negative, and written thus:  $-a : -\frac{3}{2}b : -3c$ . And for the faces in the other octants, the signs of such of the intercepts are negative as occur along the axes on the negative side of the centre.

If a face be parallel to any axis, its intercept on that axis is infinitely long, and its coefficient is  $\infty$ . For instance, if the face were parallel to the vertical axis the above symbol would become  $a : \frac{3}{2}b : \infty c$ .

These symbols of Weiss are of truly scientific character, and an accurate expression of the relative intercepts cut off from the axes by the various faces, but they are too long to be convenient symbols for the marking of crystal faces, either in a drawing of the crystal or its stereographic projection.

**Millerian Notation.**—It is much more convenient not to label the face directly with the intercepts themselves, but to divide the latter by the highest number among the three, so that the other two will become fractional parts, and then to take the denominators of these fractions as the indices of the face, when the numerators are  $a$ ,  $b$ , and  $c$  respectively. In other words, the unit intercept becomes the longest according to this method of notation, instead of the shortest as in the case of the Weiss method. It is equivalent to moving the face parallel to itself towards the centre until one of the intercepts becomes identical with that of the primary parametral face, and the other two intercepts lie within the unit values, as shown by the broken-and-dotted lines H'K'C in Fig. 41; it will be remembered that in this diagram ABC represents the unit face the intercepts of which are  $a$ ,  $b$ ,  $c$ , that HKL represents the face  $o''$  of the potassium sulphate crystal investigated in the last chapter, the intercepts of which are  $2a : 2b : 3c$ , and that ABL' represents the same face but moved up parallel to itself towards the centre until the intercepts are expressed in their lowest terms  $a : b : \frac{3}{2}c$  and the first two become  $1a$  and  $1b$ . Moving it now still further towards the centre until the largest intercept, that on the  $c$  axis, has become  $1c$  and the face cuts the axis

at C itself, so that L (of the general facial cognomen HKL) is coincident with C, the other two intercepts H' and K' will obviously be fractional parts of OA and OB respectively, namely, dividing  $2a : 2b : 3c$  by 3, the highest figure among them :

$$OH' = \frac{2}{3}a, OK' = \frac{2}{3}b, OC = c;$$

that is, the symbol becomes :

$$\frac{2}{3}a : \frac{2}{3}b : c, \text{ or } \frac{a}{\frac{3}{2}} : \frac{b}{\frac{3}{2}} : \frac{c}{1}.$$

The symbols taken to represent the face are these denominators  $\frac{3}{2}, \frac{3}{2}, 1$ , or multiplying them by 2 to get rid of the fractions : 3, 3, 2. These latter three numbers are the Millerian "indices" of the face, and they are written as a symbol within brackets, thus : (332). The brevity and general convenience of such a symbol will be at once apparent.

The "symbol" of a face is therefore an expression written within brackets thus :—(hkl), where *h*, *k*, *l* are the "indices," these latter being three numbers such that

$$\begin{array}{ccc} a & b & c \\ \hline h' & k' & l' \end{array}$$

are the intercepts made by the face on the axes.

Suppose we take another example, in which all three indices are different, say a face the intercepts of which are  $a : 2b : 4c$ . Dividing by the highest number present, 4, we get  $\frac{a}{4}, \frac{b}{2}, \frac{c}{1}$ , and the indices will consequently be (421). This is the **Millerian system of crystallographic notation**, so called because it was adopted by W. H. Miller, Professor of Mineralogy at Cambridge, in the year 1839, in his historic *Treatise on Crystallography*. It had already been previously suggested by the Rev. Dr. Whewell, but the great work of Professor Miller first brought it into prominence. It is the notation that will be employed throughout this book.

**Symbol of a Form and of its Individual Faces.**—The indices of the other faces of the same form will be the same, except that the order in which the numbers occur may be different (as in the cases of the forms of the cubic system other than the primary), and that whenever the intercept is measured along the negative side of the origin (OX', OY', or OZ' in Figs. 39-41) a negative sign is placed over the number. Thus, if the *o*" face referred to be that of the lower-left-front octant of the crystal of potassium sulphate, its indices will be ( $\bar{3}\bar{3}\bar{2}$ ), as the intercepts occur along the negative parts of the *b* and *c* axes, but along the positive part of the *a* axis.

When the symbol is written in the ordinary kind of simple brackets given above, the indices are intended to be those of a face, and if there are no negative signs above any of the numbers, it means the face in the top-right-front octant. In order to indicate the whole form of eight (or more in the higher systems), four or two faces, the symbol of this same face is used, but is placed within a pair of brackets of the type { thus : {332}.

**General Relationship of Crystal Axes, Parameters, Intercepts, and Indices.**—These relationships may now be summarised as follows. The italic letters  $a$ ,  $b$ ,  $c$  represent the axes of the crystal, of definite relative lengths, and these lengths or parameters are determined by the intercepts made along the directions of the axes by the inclined face which is chosen as the unit, parametral, or primary face ABC (one of the eight possible faces of the primary octahedral or bi-pyramidal solid), so that  $OA = a$ ,  $OB = b$ ,  $OC = c$ . The letters  $a$ ,  $b$ ,  $c$  thus represent at the same time the directions of the axes, their relative lengths (expressed by the axial ratio  $a : b = 1 : c$ ), and the parametral intercepts (intercepts made on the axes by the parametral or primary inclined plane). These same italic letters are also used in crystallography to represent the three fundamental faces (and their parallel faces) chosen for axial planes, the two  $a$  faces being those intersected by the back-to-front  $a$  axis, the pair of  $b$  faces by the lateral  $b$  axis, and the two  $c$  faces (generally termed the basal pinakoid) being cut by the  $c$  axis; the incidence of the axis on the face is rectangular (normal) if the face be a plane of symmetry. This double use of these three first letters of the alphabet is not really confusing, but rather a convenience, provided it is always clearly indicated whether a fundamental face or an axis is being referred to; if a face, the letter is generally accompanied by its indices, thus:  $a(100)$ , or  $a = (100)$ , so that no ambiguity is possible.

No general agreement has yet been arrived at as to the letter by which the faces of the primary parametral form  $\{111\}$  shall be labelled. The author generally employs the letter  $o$ , as in Fig. 40, which reminds one that the form is of octahedral character.

Any other face than the four primary faces is generally referred to in diagrams (Fig. 41) as HKL, and is distinguished in the drawing, description, and stereographic projection of the crystal by an italic labelling letter, common to the form, and by the symbol  $\{hkl\}$ , its form of eight (or more in the systems higher than the rhombic), four or two faces being  $\{hkl\}$ , in which :

$$h = \frac{OA}{OH} = \frac{a}{OH}, \quad k = \frac{OB}{OK} = \frac{b}{OK}, \quad l = \frac{OC}{OL} = \frac{c}{OL},$$

or as it is more usually written, to give the values of the intercepts OH, OK, OL :

$$OH = \frac{OA}{h} = \frac{a}{h}, \quad OK = \frac{OB}{k} = \frac{b}{k}, \quad OL = \frac{OC}{l} = \frac{c}{l}.$$

The three indices  $h$ ,  $k$ ,  $l$  consequently define the position of the face completely, when the parameters  $OA$ ,  $OB$ ,  $OC$  ( $a$ ,  $b$ ,  $c$ ) are known. The values can be reduced to their simplest form, in which one of them = 1 or some other small number (2 in the case of the  $o''$  face of the potassium sulphate crystal), by multiplying or dividing all three indices by the same positive whole number; for, as already shown, this is only equivalent to a translation of the face parallel to itself, which has no effect on the elements of the structure.

**Indices of the three Axial Planes.**—Each face of the three fundamental



pairs of faces parallel to the axial planes, that is to say, those faces which were chosen for axial planes, will obviously be cut by one axis only, as shown in Fig. 40, and will be parallel to the other two axes, for these latter are parallel to its edges of intersection with the two other axial planes; hence, to use the ordinary geometrical convention, it will only meet those two other axes at an infinite distance. When, however, the intercept becomes  $\infty$ , the index becomes 0, thus, if  $OH = \infty = \frac{a}{h}$ , then

$$h = \frac{a}{\infty} = 0.$$

Hence the symbol of a face parallel to two axes will have in it two ciphers, and the other index will be 1. The symbol of the face  $a$  will be (100), because it cuts the forward axis  $a$  only, that of the face  $b$  will be (010) because it cuts the lateral axis  $b$  only; and that of the face  $c$ , the basal plane, will be (001) because it cuts the vertical axis  $c$  only. The faces parallel to these will be ( $\bar{1}$ 00) (0 $\bar{1}$ 0), and (00 $\bar{1}$ ).

**Indices of the Primary Inclined (Parametral) Faces.**—The face chosen as the fourth fundamental face ABC, which defines by its intersection with, or intercepts on, the three axes the unit lengths of those axes, will obviously have the symbol (111), its position being in the top, right-hand-front octant. The other seven faces of the form (octahedral in character) will be ( $\bar{1}$ 11) for the face in the top-front-left octant, ( $\bar{1}\bar{1}$ 1) for that in the top-back-left octant, and ( $\bar{1}$ 1 $\bar{1}$ ) for the face in the top-back-right octant. There will be four similar faces of like indices in the four lower octants, the symbols only differing by having also a negative sign over the third 1, to mark the fact that the vertical  $c$  axis is cut in the lower negative half.

In actual practice, if it should happen, as is not infrequently the case, that the crystal has no facial plane developed inclined to all three axes, a pair of faces, each of which is inclined to two of the three axes but parallel to the third axis, may be taken to determine the axial lengths, provided two such planes are present, and that the axis to which parallelism occurs is a different one in the two cases. Thus a combination of any two which may be developed of the primary faces (110), (011), (101) serves to determine the relative axial lengths, in the absence of the parametral facial plane (111) itself.

**Relationship and Mutual Conversion of the Symbols of Weiss and Miller.**—The elegance of Miller's method, the brevity of the symbol, rendering it eminently suitable for the labelling of crystal faces either on large specimens or on drawings of the crystals, and its direct application to the stereographic projection and the methods of calculating by spherical trigonometry, have all combined to bring it into general use, and it is now the almost universally accepted method of notation, and has been employed by Professor von Groth as the notation of the unique publication of the subject, the *Zeitschrift für Krystallographie*. The symbols of Weiss, however, are the direct expression of the intercepts, and it is of some consequence to be able to convert the one kind of symbol into the other, even if only for the purpose of finding the intercepts themselves, from the Millerian indices, when it is desired to draw the crystals to

scale according to the conventional method to be hereafter described in Chapter XXV.

In order to convert the Millerian symbol ( $hkl$ ) into Weiss notation, we multiply each term of the expression for the intercepts

$$\frac{a}{h} : \frac{b}{k} : \frac{c}{l}$$

(in which  $h, k, l$  are the Millerian indices and  $a, b, c$  are the axial intercepts of the primary face, that is, the unit lengths of the three axes) by the product of  $h \cdot k \cdot l$ ; the ratios then become

$$kla : hlb : hkc.$$

That is, we multiply together the two other Millerian indices in order to get the Weiss coefficient of any one axis, reducing, if necessary, the coefficients thus found to their simplest relation.

For example, the Weiss symbol for the face represented in Millerian notation by (123) is  $6a : 3b : 2c$ , or simpler,  $3a : \frac{3}{2}b : c$ .

It is well to remember that Weiss's intercept-coefficients are directly proportional, and Miller's indices inversely proportional, to the lengths of the intercepts made by the face under consideration on the crystal axes. The highest intercept-coefficient consequently corresponds to the lowest index, and *vice versa*.

As an example of the converse process, suppose the Weiss expression for a face to be  $a : \frac{3}{2}b : \frac{1}{2}c$ . Reducing this to the form  $\frac{a}{h} : \frac{b}{k} : \frac{c}{l}$ , by dividing all through by 3, we get  $\frac{a}{3} : \frac{b}{2} : \frac{c}{6}$ . The Millerian symbol is there-

fore (326). Or taking once more the face  $o''$  of potassium sulphate, which has the Weiss intercept-coefficients  $2a : 2b : 3c$ , we proceed to reduce the latter expression to the form  $\frac{a}{h} : \frac{b}{k} : \frac{c}{l}$  by dividing all through by 6, when we get  $\frac{a}{3} : \frac{b}{3} : \frac{c}{2}$ . The Millerian symbol is consequently (332).

A safe rule for the reduction of the Weiss expression  $ma : nb : rc$  to the Millerian expression  $\frac{a}{h} : \frac{b}{k} : \frac{c}{l}$  is to divide the former by the product  $mnr$ , that is, to get the Millerian index for any axis we multiply together the intercepts on the other two; then if the resulting values of  $h, k, l$  admit of further simplification by means of a common divisor, we so simplify them. Using this rule in the case of the  $o''$  face just referred to,  $m \cdot n \cdot r = 12$ , and  $h, k, l$  work out respectively to 6, 6, 4. These will simplify by dividing by 2, which thus reduces them to 3, 3, 2.

**The Facial Form-Symbols of Naumann.**—A modified and more or less arbitrary form of Weiss notation was for many years very popular for the description of crystal faces. It was devised by C. F. Naumann, and propagated in his popular *Elemente der Mineralogie*. It combines the Weiss parametral values with certain arbitrary signs, which differ for the various crystal systems. The general symbol corresponding to the Millerian  $hkl$ , or to the Weiss expression written in the form  $ma : b : nc$ ,

is  $mPn$  in the tetragonal and rhombic systems, where the axes are rectangular, the  $P$  standing for primary pyramid. In the monoclinic system, in which one of the axes is oblique, the  $P$  is marked on its stem with an oblique stroke, thus  $P$ , if the face belong to a clino-form, or a rectangular one for a face of the orthozone or other ortho-form, thus  $P$ . In the rhombic and triclinic systems the  $P$  is marked over the top with a straight stroke, thus  $\bar{P}$ , or with a little arched (inverted) accent, thus  $\tilde{P}$ , according as the face is parallel to the macro- or brachy-diagonal, the longer  $b$  axis or the shorter  $a$  axis of the crystal. The signs  $\backslash$  and  $-$ ,  $-$  and  $\cup$ , are also employed for pyramidal or prismatic forms other than the primary, to indicate whether they are on the clino- or ortho-, macro- or brachy-, side of the primary form of the series. In the cubic system, where the primary pyramid  $P$  of Millerian indices  $\{111\}$  is replaced by the octahedron, the letter  $O$  is used instead of  $P$ , so that the general form in this system is  $mOn$ . When the face is parallel to a crystallographic axis, instead of intercepting it,  $m$  or  $n$  is replaced by the sign of infinity  $\infty$ . Thus the cube faces are all marked  $\infty O \infty$ . The primary prism is  $\infty P$ , or  $\infty O$  in the cubic system, this latter symbol being that of the rhombic dodecahedron. The primary pyramid itself is  $O$  or  $P$ , and the basal plane is always  $oP$ . A face such as a brachydomal prism of the rhombic system is  $m\tilde{P}\infty$ , for instance.

These symbols of Naumann are now quite obsolete for the purposes of accurate crystallography. They are interesting, however, historically, and are still often seen in the older text-books and sometimes in museums marked on the faces of large mineral crystals. They had, indeed, a certain value for descriptive purposes, when once the arbitrary signs and symbols had been thoroughly mastered, being short, and one symbol covering the whole of the faces of a form, that is, the whole of the faces present of equal value as regards the symmetry.

To provide for the event of the necessity arising to study any crystals thus marked, or to unravel the symmetry of crystals described in the older memoirs or treatises, a list of the symbols of all the principal forms of all seven crystal systems in Naumannian notation, opposite the corresponding Millerian symbols, now follows. It is given here, although the seven crystal systems are not described in detail until later Chapters (X.-XXII.), as it will not be necessary again to refer to the Naumannian symbols. It should be considered as a table of reference.

COMPARATIVE TABLE OF MILLERIAN AND NAUMANNIAN SYMBOLS.

*Cubic System.*

Miller.	Naumann.	Miller.	Naumann.
$\{100\}$	$\infty O \infty$ (cube)	$\{hkk\}_{(h>k)}$	$mOm$ (icositetra-
$\{110\}$	$\infty O$ (rhombic dodecahedron)	$\{hhl\}_{(h>l)}$	hedron)
$\{111\}$	$O$ (octahedron)		$mO$ (triakis octahedron)
$\{hko\}$	$\infty On$ (tetakis hexahedron)	$\{hkl\}$	$mOn$ (hexakis octahedron)

The so-called "hemihedral" and "tetartohedral" forms are indicated in Naumannian notation by halving or quartering the symbol, and preceding it by the positive or negative sign and, if there are right and left varieties, adding after it the letter



$r$  or  $l$ . Thus, the two (*in situ*) hexakis tetrahedra are  $+\frac{mOn}{2}$  and  $-\frac{mOn}{2}$ ; the two (*in situ*) simple tetrahedra are  $+\frac{O}{2}$  and  $-\frac{O}{2}$ ; the two (*in situ*) triakis tetrahedra are  $+\frac{mOm}{2}$  and  $-\frac{mOm}{2}$ ; the two (*in situ*) deltoid dodecahedra are  $+\frac{mO}{2}$  and  $-\frac{mO}{2}$ ; the left pentagonal icositetrahedron is  $\frac{mOn}{2}l$  and the right pentagonal icositetrahedron is  $\frac{mOn}{2}r$ ; the right positive tetrahedral pentagonal dodecahedron is  $+\frac{mOn}{4}r$ , and the left negative tetrahedral pentagonal dodecahedron is  $-\frac{mOn}{4}l$ . To distinguish the two dyakis dodecahedra and the two pentagonal dodecahedra, the two special solids of the pyrites class 30, another convention was employed, that of enclosing the symbol within large square brackets, the two forms being written  $\left[\frac{mOn}{2}\right]$  and  $\left[\frac{\infty On}{2}\right]$  respectively, the two varieties (*in situ*) of each being distinguished by  $+$  or  $-$  signs, or the letters  $r$  and  $l$ , according to the nomenclature adopted ( $+$  and  $-$  were usually employed). Similar devices are also employed in the other following six systems to indicate the classes of lower than the full systematic symmetry.

#### Tetragonal System.

Miller.	Naumann.	Miller.	Naumann.
$\{100\}$	$\infty P\infty$	$\{hOl\}$	$mP\infty$
$\{001\}$	$oP$	$\{hko\}$	$\infty Pn$
$\{110\}$	$\infty P$	$\{hhl\}$	$mP$
$\{101\}$	$P\infty$	$\{hkl\}$	$mPn$
$\{111\}$	$P$		

#### Rhombic System.

Miller.	Naumann.	Miller.	Naumann.
$\{100\}$	$\infty \bar{P}\infty$	$\{hkl\}_{h>k}$	$m\bar{P}n$
$\{010\}$	$\infty \bar{P}\infty$	$\{hkl\}_{h<k}$	$m\bar{P}n$
$\{001\}$	$oP$	$\{hOl\}$	$mP\infty$
$\{110\}$	$\infty P$	$\{OkI\}$	$m\bar{P}\infty$
$\{101\}$	$\bar{P}\infty$	$\{hko\}_{h>k}$	$\infty \bar{P}n$
$\{011\}$	$\bar{P}\infty$	$\{hko\}_{h<k}$	$\infty \bar{P}n$
$\{111\}$	$P$	$\{hkh\}_{h>k}$	$\bar{P}n$
$\{hhl\}_{h>l}$	$mP$	$\{hkl\}_{h<k}$	$\bar{P}n$

The special marks of the Naumannian notation for this system are the long sign  $-$  to indicate that the form belongs to a macrodiagonal series, and  $\infty$  to signify brachydiagonal character, both signs being placed over the  $P$ . Thus the macropinakoid is  $\infty \bar{P}\infty$  and the brachypinakoid  $\infty \bar{P}\infty$ .

#### Monoclinic System.

Miller.	Naumann.	Miller.	Naumann.
$\{100\}$	$\infty P\infty$	$\{hkl\}_{h>k}$	$-mPn$
$\{010\}$	$\infty P\infty$	$\{hkl\}_{h>k}$	$+mPn$
$\{001\}$	$oP$	$\{hkl\}_{h<k}$	$-mPn$
$\{110\}$	$\infty P$	$\{hkl\}_{h<k}$	$+mPn$
$\{101\}$	$-P\infty$	$\{hkh\}_{h>k}$	$-Pn$
$\{10\bar{1}\}$	$+P\infty$	$\{hkh\}_{h>k}$	$+Pn$
$\{011\}$	$P\infty$	$\{hkk\}_{h<k}$	$-Pn$
$\{111\}$	$-P$	$\{hkk\}_{h<k}$	$+Pn$
$\{1\bar{1}1\}$	$+P$	$\{hOl\}$	$-mP\infty$
$\{hhl\}$	$-mP$	$\{hOl\}$	$+mP\infty$
$\{hhl\}$	$+mP$	$\{OkI\}$	$mP\infty$
		$\{hko\}_{h>k}$	$\infty Pn$
		$\{hko\}_{h<k}$	$\infty \bar{P}n$

The special marks of the Naumannian symbols for the monoclinic system are the straight stroke on the stem of the P, namely P, to indicate an ortho-form, and the inclined stroke P, to indicate a clino-form.

### Triclinic System.

Miller.	Naumann.	Miller.	Naumann.
$\{100\}$	$\infty \bar{P} \infty$	$\{0kl\}$	$m, \bar{P}' \infty$
$\{010\}$	$\infty \bar{P} \infty$	$\{0kl\}$	$m, \bar{P} \infty$
$\{001\}$	$oP$	$\{hk0\}$	$\infty \bar{P}' n$
$\{110\}$	$\infty P'$	$\{hk0\}$	$\infty \bar{P} n$
$\{1\bar{1}0\}$	$\infty \bar{P}' P'$	$\{hk0\}$	$\infty \bar{P}' n$
$\{111\}$	$P'$	$\{hk0\}$	$\infty \bar{P} n$
$\{1\bar{1}1\}$	$\bar{P}$	$\{hkl\}$	$m \bar{P}' n$
$\{1\bar{1}\bar{1}\}$	$\bar{P}$	$\{hkl\}$	$m \bar{P} n$
$\{111\}$	$\bar{P}$	$\{hkl\}$	$m \bar{P} n$
$\{hhl\}$	$m \bar{P}'$	$\{hkl\}$	$m, \bar{P} n$
$\{hhl\}$	$m' \bar{P}$	$\{hkl\}$	$m \bar{P}' n$
$\{hhl\}$	$m \bar{P}$	$\{hkl\}$	$m \bar{P} n$
$\{hhl\}$	$m, \bar{P}$	$\{hkl\}$	$m \bar{P} n$
$\{h0l\}$	$m' \bar{P}' \infty$	$\{hkl\}$	$m \bar{P} n$
$\{h0l\}$	$m, \bar{P} \infty$	$\{hkl\}$	$m, \bar{P} n$

The macro- and brachy-signs – and  $\infty$  are employed in the triclinic as in the rhombic system. The only new sign introduced is the accent ' to indicate the octant, whether right or left and upper or lower octant.

### Hexagonal System.

Bravais-Miller.	Naumann.	Bravais-Miller.	Naumann.
$\{0001\}$	$oP$	$\{11\bar{2}2\}$	$P2$
$\{1010\}$	$\infty P$	$\{h0hl\}$	$m \bar{P}$
$\{11\bar{2}0\}$	$\infty P2$	$\{kkhl\}$	$m P2$
$\{10\bar{1}1\}$	$P$	$\{hk0\}$	$\infty Pn$
$\{11\bar{2}1\}$	$2P2$		
		$\{hkl\}$	$m \bar{P} n$
			$m = \frac{h}{l}$
			$n = \frac{h}{k}$

No special signs are employed, the symbols being analogous to those of the tetragonal system.

### Trigonal System.

Miller.	Naumann.	Miller.	Naumann.
$\{111\}$	$oR$	$\{pqr\}$	$mRn$
$\{2\bar{1}1\}$	$\infty R$	$\{p\bar{q}r\}$	$\infty Pn$
$\{10\bar{1}\}$	$\infty P2$	$\{p\bar{q}\bar{q}\}$	$mR$
$\{100\}$	$R$		
$\{122\}$	$-R$		

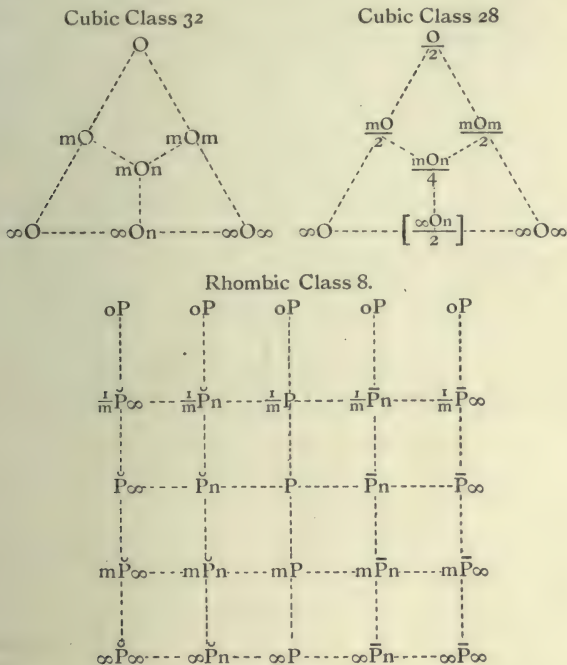
For the three classes of this system in which the rhombohedron is the principal form, the P of the other classes and of those of the hexagonal system is replaced by R. The other classes, of which the trigonal prisms and pyramids are characteristic, are treated as if they were part of the hexagonal system, both trigonal and hexagonal systems having been formerly considered as one system, the hexagonal.

As both Bravais-Millerian and Millerian symbols are given in Chapter XXII., in considering the forms and classes of the trigonal system, any difficulty in finding the Naumannian symbol should be resolved with the aid of these two comparative tables for the hexagonal and trigonal systems, remembering that R instead of P is used when rhombohedral forms are concerned.

*Naumannian Diagram of Form Relationship.*

The relationship of the various forms, and their derivation or evolution from one another in series, may be clearly exhibited for each system and class by a diagram of the character typified by the following three examples. The first, of triangular shape, is that for the holohedral forms of the cubic system, class 32. The second similar diagram refers to the tetrahedral pentagonal dodecahedral class 28 of the cubic system, and brings in "hemihedral" forms and one "tetartohedral" form, that which gives its name to the class. The third is the diagram, rectangular in shape, for the holohedral forms of the rhombic system, class 8.

If the first two vertical columns and also the sign  $-$  are omitted, this third diagram also represents accurately the holohedral class of the tetragonal system, class



15. If the diagram stand as it is, except that the signs  $-$  and  $\cup$  over the  $P$  be changed for the signs  $-$  and  $\setminus$  placed on the stem of the  $P$ , the holohedral class of the monoclinic system is represented, class 5. The forms in the second, third, and fourth horizontal rows, except the first number in each case, should also have  $\pm$  marked in front of them.

**The Law of Rationality of Intercepts or Indices.**—We now come to one of the most remarkable and important facts in crystallography. After having fixed the elements of the crystal and determined by reference to the primary form the symbols of all other faces developed on the crystal, from the data afforded by the angular measurements, we find that, provided our measurements have been accurate and the crystals are of the desirable high state of perfection, **the whole of the symbols thus**



obtained consist of small whole numbers, generally not larger than 3 or 4, and very rarely indeed amounting to 6 or more, which latter only happens on crystals such as those of natural minerals which are extraordinarily rich in faces. In other words, taking the now generally accepted Millerian notation for greater convenience, the values of the indices  $h$ ,  $k$ ,  $l$  can always be expressed as small whole numbers, chiefly 1, 2, 3, or 4. This is the law of "rationality of indices," and it can be briefly expressed in the statement: "The indices of any and every face on a crystal are three small whole numbers."

This important law is equally true, however, of intercepts as of indices, as will be obvious from the close relationship between them. Expressing the intercepts by the Weiss notation  $ma : nb : rc$ , the law requires that  $m$ ,  $n$ , and  $r$  shall be whole numbers.

The law in its complete form may be expressed in the following two statements, the first referring to intercepts and the second to indices:—

**The intercepts on the crystal axes, made by any face of the crystal, are such as can be expressed as rational multiples of the parametral unit lengths of those axes, as determined by the intersection of those axes with the primary face which has been chosen as the parametral plane.**

If  $OA$ ,  $OB$ ,  $OC$  be the crystal axes intersecting at  $O$  in the centre of the crystal, and parallel to the edges of the three faces chosen as the fundamental faces and directions of the axial planes, and if their respective lengths be  $a = OA$ ,  $b = OB$ ,  $c = OC$ , as determined by the intercepts made upon them by a fourth face chosen as the primary or parametral face, and if, further,  $H$ ,  $K$ ,  $L$  be the points at which the axes are met by any other facial plane developed on the crystal, then in the expressions

$$OH = \frac{a}{h}, \quad OK = \frac{b}{k}, \quad OL = \frac{c}{l}$$

$h$ ,  $k$ , and  $l$  are small whole numbers.

This law is strictly true whichever three faces meeting in three edges are chosen as the axial planes, but for obvious reasons, when symmetry is developed in the crystal, such faces as are parallel to the planes of symmetry are chosen for the axial planes. Whichever three faces are chosen, they form with their parallel faces the six faces of a closed figure having twelve edges, which is the cube in the case of highest symmetry, a rectangular block in the case of an intermediate type of symmetry such as the orthorhombic crystal of potassium sulphate already considered, or a similar block but without any right angles in the general case of triclinic crystals in which no planes of symmetry are developed, as shown in Fig. 40.

The subject of the proper choice of axial planes and of the proper arrangement in space of the three planes chosen, that is, the correct "setting up" of the crystal, is so important from the point of view of the internal structure of crystals, that a special section will be devoted to it in a later chapter (XXXIV.), after the various types of symmetry and the cleavage of crystals have been discussed.

## CHAPTER VI

### ZONES, THEIR TEACHING, AND REPRESENTATION IN STEREOGRAPHIC PROJECTION

**Symbol of a Zone.**—The fact that the faces of a crystal are arranged in zones, each of such a character that the successive pairs of adjacent faces composing it meet in edges which are all parallel to each other and to the zone axis, was elicited in Chapter IV. by the practical investigation on the goniometer of the typical crystal of potassium sulphate. Such faces belonging to the same zone are said to be “cozonal” or “tautozonal” (from *ταὐτό*, “the same”). It was also seen that the adjustment to the axis of the goniometer of any two faces of the zone other than parallel faces brought about the automatic adjustment of the whole zone of faces. Two faces are consequently adequate to determine a zone, and it is found convenient, and of great help in ascertaining the indices of other faces, both of the same and of other zones, that the indices of these two determining faces should be combined so as to afford us a symbol of the whole zone. To distinguish a zone symbol from that of a face, it is always written in square brackets, thus: [431]. The indices of the zone are found as follows: Let the symbols of the two determining faces be  $(hkl)$  and  $(h'k'l')$ . We write the indices of each symbol twice over in the same horizontal line, arrange those of one symbol below those of the other, and cross-multiply (the method of determinants) all except the two end pairs, thus:

$$\begin{array}{c|cccc|c} h & k & l & h & k & l \\ & \times & \times & \times & & \\ h' & k' & l' & h' & k' & l' \end{array}$$

Then, if  $[uvw]$  be the symbol of the zone, the three indices  $u, v, w$  are found from the above cross-multiplication by taking the difference of the products of each adjacent pair of cross-multiplied facial indices. That is,

$$u = kl' - lk'; \quad v = lh' - hl'; \quad w = hk' - kh'.$$

The values thus found for the indices of a zone may be reduced to their simplest relationship by dividing them all by any common divisor, or they may all be multiplied by any one and the same number, or all their signs may even be changed, without altering their nature as indices of the zone. This last fact regarding the sign will be obvious, for the

sign simply depends on which of the two facial indices is written above and which below the other.

The meaning of zone-indices is quite different from that attached to face-indices. The points on the axes given by the face-indices ( $hkl$ ) are obviously points in the face, and the three lines joining them lie in the face; it has also to be remembered that the intercept-lengths are inversely as the indices, that is,  $\frac{a}{h} : \frac{b}{k} : \frac{c}{l}$ . On the other hand, the zone-indices

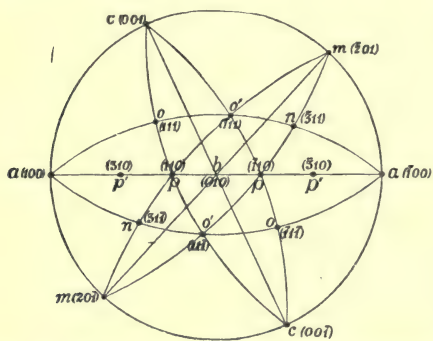
$[uvw]$  give directly the points on the axes, and these points, by their distances from the origin, determine the lengths of the edges of a parallelepiped (the directions of these edges being those of the three axes), the diagonal of which from the origin (axial centre) is parallel to the zone-axis and to the edges of intersection of the tautozonal faces. Thus, for instance,

the face represented by the indices (321) has intercepts  $\frac{a}{3}, \frac{b}{2}, c$ , or  $2a, 3b, 6c$ ; whereas the indices  $[321]$  represent a zone the axis of which is the diagonal, from the origin, of a parallelepiped the edges of which are  $3a, 2b, c$ .

A zone axis cannot be perpendicular to a possible face of the crystal, except the latter belong to the cubic system, in which system every zone-axis is perpendicular to a possible face, and in a few special cases, such as when the zone-axis is parallel or perpendicular to the principal axis in the tetragonal, trigonal or hexagonal systems, or when it is perpendicular to a symmetry plane.

**Use of Zone Symbols in finding Facial Indices.**—The task of finding the indices of a subsidiary face on a crystal is often greatly facilitated

by the fact that the face is situated at the intersection of two zones, and is thus common to the two zones. For the symbol of such a face is at once given by the cross-multiplication of the symbols of the two zones, in the same manner as that just employed for the finding of a zone symbol. For instance, in a crystal of ammonium selenate belonging to the monoclinic system measured by the author, a certain face  $n$  was situated at





$$\begin{array}{r|rrrr|l}
 \bar{1} & 0 & 0 & \bar{1} & 0 & 0 \\
 & \times & \times & \times & & \\
 \bar{1} & 1 & 1 & \bar{1} & 1 & 1 \\
 \bar{2} & 0 & 1 & \bar{2} & 0 & 1 \\
 & \times & \times & \times & & \\
 \bar{1} & 1 & 0 & \bar{1} & 1 & 0 = [\bar{1}\bar{1}\bar{2}]
 \end{array}$$

Then by cross-multiplication of the zone symbols we obtain the symbol of the face, as follows :

$$\begin{array}{r|rrrr|l}
 0 & 1 & \bar{1} & 0 & 1 & \bar{1} \\
 & \times & \times & \times & & \\
 \bar{1} & \bar{1} & \bar{2} & \bar{1} & \bar{1} & \bar{2} \\
 & & & & & \\
 & & & & & = (\bar{3}\bar{1}\bar{1})
 \end{array}$$

The face  $n$  has, therefore, the indices  $(\bar{3}\bar{1}\bar{1})$ .

That the signs of the indices are merely a function of the order in which the two zone symbols are taken will be at once apparent, for if we place the  $[\bar{1}\bar{1}\bar{2}]$  zone on the top line instead of the bottom line, and the  $[0\bar{1}\bar{1}]$  zone below, we shall obtain  $(\bar{3}\bar{1}\bar{1})$  for the indices of the face  $n$ . Hence, the signs may be changed (provided all three in the symbol are so changed) without causing the indices to cease to represent the plane of the face. As a matter of fact, the two sets of signs correspond to the two parallel faces on opposite sides of the crystal, the two zones meeting twice on opposite sides of the centre. The ambiguity as to sign disappears when the position of the face as regards the octant in which it occurs is considered, for it is then obvious which of the axes will be cut by the face on the positive side and which on the negative side of the centre. There is, however, a safe rule for fixing the signs, dependent again on the occurrence of three faces in a zone. It is as follows :—

If the known indices of two faces in a zone be added together, each index of the one to that for the same axis of the other, the sum is the symbol of a face lying between the two faces in question, and in the same zone. In other words, it affords the indices of a third face in the zone, replacing the edge in which the two faces under consideration meet.

For instance, in the case of the example just given, and illustrated in Fig. 42, if we add together the indices of the faces  $m$  and  $p$  we get :

$$\begin{array}{r}
 \bar{2}01 \\
 \bar{1}\bar{1}0 \\
 \hline
 \bar{3}\bar{1}\bar{1}
 \end{array}$$

and  $(\bar{3}\bar{1}\bar{1})$  is the symbol of the face  $n$  with its correct sign.

We cannot adopt this rule to give us with certainty the indices themselves, however, but only in order to fix the sign ; because there may be several faces intermediate between the two faces the symbols of which are known, and the result may not be the particular one required. The cross-multiplication of the two zone-symbols must be resorted to, in order indubitably to obtain the indices, as has just been described. The case before us (Fig. 42) is an excellent example, for if we add the indices

of the two faces  $o'$  and  $a$  of the second zone, we get the symbol  $(211)$ , which is not that of the face  $n$ , but of another face in the zone between  $n$  and  $o'$ , its pole being in fact at the point where the diameter  $mm$  crosses the zonal arc. Indeed, if we add together the indices of  $m = (201)$  and of  $b = (010)$  the pole at the centre (that of the undeveloped clino-pinakoid), we get  $(211)$ .

One more use of the zone symbol  $[uvw]$  is to verify whether a face  $(hkl)$  belongs to a particular zone or not. For when it does,

$$hu + kv + lw = 0.$$

Taking again the same example, the symbol of the zone  $mp$  is  $[\bar{1}\bar{1}\bar{2}]$ , and that of the face  $n$  is  $(311)$ , and

$$hu + kv + lw = \bar{3} \times \bar{1} + 1 \times \bar{1} + 1 \times \bar{2} = 3 - 1 - 2 = 0.$$

Also the symbol of the zone  $ao'$  is  $[01\bar{1}]$ , and

$$hu + kv + lw = \bar{3} \times 0 + 1 \times 1 + 1 \times \bar{1} = 0 + 1 - 1 = 0.$$

Thus the face  $n$  does lie in the two zones  $mp$  and  $ao'$ .

Two further facts follow from the above considerations, namely:  
**A plane which is common to two zones is always a possible face of the crystal ; and all the faces of even the most highly developed crystal (rich in faces) are connected together in zones.**

Moreover, as all the zone symbols are got by cross-multiplication of rational facial indices, the zone symbols themselves are rational ; consequently, the indices of any other face, obtained by the cross-multiplication of the zone-symbols of two zones to which the face is common, must also be rational. Hence : **All the faces which are indicated as possible by constructing all possible zone circles on a stereographic projection, and marking their intersections by dots to represent facial poles, must be identical with the faces indicated as possible by taking all the possible combinations of rational indices.**

The law of rational indices is, therefore, implied in the statement that **all the faces of a crystal lie in zones constructed from four of its faces, no three of which lie in the same zone ; for all the faces of a crystal have simple rational indices referred to its axes, which are determined by those four faces, three determining the directions of the axes and the fourth their lengths.** In such a form it is known as the ‘zone law.’

We can now take one further concluding step in the extremely valuable teaching of zone relationships, and one which is of untold value in the calculation of crystal angles and crystal elements. It is given in the succeeding paragraphs.

**Law of Rational Double-Ratios, or Anharmonic Ratio of Four Poles in a Zone.**—If  $a, b, c, d$  be four faces of a crystal lying in one and the same zone, the double-ratio (anharmonic ratio) of the sines of the angles between them is a rational number, which is expressed by the corresponding double-ratio of the indices of the four faces. This far-reaching law has one immediate consequence, namely, that there can only be three faces in a zone inclined at any angles whatsoever ; for any fourth face also making

any angle whatsoever would make the value of the double-ratio irrational. Consequently, this fourth angle must have a definite value, dependent on the values assumed by the other three angles, that is, on the position taken up by the three faces first considered. The formula in which the law is mathematically expressed, and which is an exceedingly simple one, enables us to determine either the fourth angle, given the indices of all four faces and the angles between three of them, or the indices of the fourth face, given the four angles and the indices of three faces. This formula may be written :

$$\frac{\sin(a:b) \cdot \sin(d:c)}{\sin(a:c) \cdot \sin(d:b)} = \frac{(hkl) \text{ of } a \times (hkl) \text{ of } b}{(hkl)_a \times (hkl)_c} \cdot \frac{(hkl)_d \times (hkl)_e}{(hkl)_d \times (hkl)_b}$$

By "multiplication" of the indices on the right-hand side of the equation is to be understood "cross-multiplication" (the method of determinants) in a sense to be presently fully explained.

This principle of the anharmonic ratio of four poles in a zone affords us the indispensable connection between the indices of the faces (on the right in the equation) and the measured interfacial angles (on the left), which latter are the practical means open to us of defining the relative positions of the facial planes of crystals. We arrive at the principle from the following considerations.

It will be remembered from the first principles of geometry that if A, B, C, D be four points on a straight line, then any one of the ratios

$$\frac{AB}{AC} \cdot \frac{DC}{DB} \text{ or } \frac{AC}{AD} \cdot \frac{BD}{BC} \text{ or } \frac{AB}{AD} \cdot \frac{CD}{CB},$$

or of the same ratios inverted, is termed an anharmonic ratio of the four points. It may be any one of the six ratios in which each point occurs once in the numerator and once in the denominator.

In the same manner, if A, B, C, D be four straight lines meeting at a common point O, as in Fig. 43, the anharmonic ratio of the sines of the angles is any one of six ratios, as before, of the type

$$\frac{\sin AOB}{\sin AOC} \cdot \frac{\sin DOC}{\sin DOB}.$$

If, now, we combine these two geometrical and trigonometrical principles, by allowing the straight line first considered to intersect the four straight lines forming the angles by their meeting at O, say in the points A, B, C, D (Fig. 43), then it is readily capable of proof that the anharmonic ratio of the four points is equal both in magnitude and sign to the corresponding anharmonic ratio of the sines of the angles, that is :

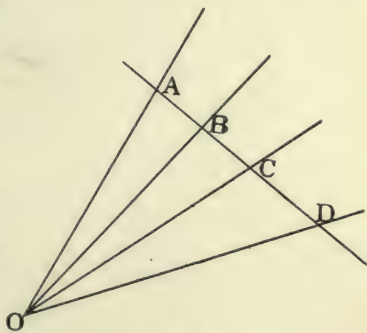


FIG. 43.



$$\frac{AB}{AC} \cdot \frac{DC}{DB} = \frac{\sin AOB}{\sin AOC} \cdot \frac{\sin DOC}{\sin DOB}$$

Care must be taken that the order of the letters is the same on each side of the equation, and that the signs are correct. For  $BA = -AB$ , and  $\sin BA = \sin(-AB) = -\sin AB$ .

Now, a precisely similar relationship holds between the indices of the faces on a crystal and the angles between those faces; and if  $a, b, c, d$  be the four faces of the crystal lying in the same zone, then:

$$\frac{\sin ab}{\sin ac} \cdot \frac{\sin dc}{\sin db} = \frac{ab}{ac} \cdot \frac{dc}{db},$$

provided  $ab, ac, dc, db$  on the right-hand side of the equation are taken to mean the products (by cross-multiplication) of the indices of the respective faces, and on the left-hand side the angles between the faces. With these significations accepted for the letters, this equation is identical with that given on the previous page as the general formula expressing the anharmonic ratio of four poles in a zone. Hence, **the anharmonic ratio of the sines of the angles between four tautozonal (cozonal) planes is equal to the anharmonic ratio of their indices.**

The immense practical utility of this formula will be at once apparent when it is remembered that the value of the anharmonic ratio of the indices is, as stated at the head of this section, a rational simple number, or simple fraction the numerator and denominator of which are low rational numbers, not generally higher than 4, and often only 2 or 3. This must be so, because of the rationality of the indices themselves. Consequently, if we know the positions of three poles in a zone, any other pole which makes the anharmonic ratio rational is that of a possible face of the crystal, and the angle made by this possible face with the other faces may be found for any rational number, corresponding to any desired or suggested indices. The angle thus obtained by calculation can then be compared with the measured angle between the actual fourth face and one of the other three faces, and the suggested indices of the fourth face thus either verified or shown to be untenable, when another likely rational number could be tried. Generally there are only two possibilities, and one or other of the two corresponding symbols will be found to yield a calculated angle which will agree with the measured angle. Or the converse use may be made of the formula, namely, knowing with certainty the indices of the fourth face, from the application of the zone rules, we may find the angle, that is, the position of the fourth face in the zone. For it may happen that this particular angle has not been measured, on account of bad reflections of the signal-image from the face in question; or if it has been measured, it may be desirable to verify the value obtained for the angle, as the reflections may have been imperfect, or at any rate of a lower order of perfection than those afforded by certain other faces, the angles between which are used as the basis of the calculations.

To illustrate the use of this important principle in practice, an example will be taken from the calculations made by the author from his measurements of the monoclinic crystals of ammonium selenate.

In the zone  $[copo'c]$ , shown in the stereographic projection, Fig. 42, and in shortened diagrammatic form in Fig. 44, there are the poles of four faces of different forms, the fifth pole being that of the  $c$  face parallel to the first and belonging to the same form. The four poles to be considered, therefore, are those of  $c=(001)$ ,  $o=(111)$ ,  $p=(110)$ , and  $o'=(1\bar{1}\bar{1})$ . The angles  $cp$  and  $po'$  were known with certainty to be respectively  $77^\circ 26'$  and  $43^\circ 16'$  from the measurements, which had been made on numerous excellent crystals, on all of which faces of the forms  $c=\{001\}$ ,  $p=\{110\}$ , and  $o'=\{1\bar{1}\bar{1}\}$  had been developed. The form  $o=\{111\}$  had been of rarer occurrence, and it was desired to check the values obtained for the angles  $co$  and  $op$  by calculation from the indisputable values of  $cp$  and  $po'$ .

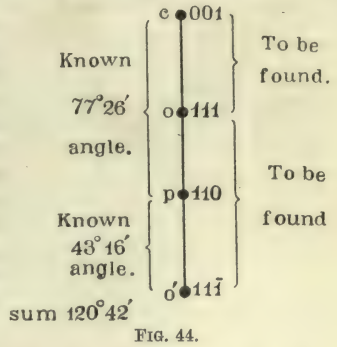


FIG. 44.

Setting down the anharmonic ratios of the sines of the angles on one side of the equation, in the order convenient for our purpose, and then the indices on the other side, over each other in pairs (so as to be conveniently placed for cross-multiplication) and corresponding to the pairs of faces forming the respective angles, all in the same order as the angles are taken, we obtain :

$$\frac{\sin co}{\sin cp} \cdot \frac{\sin o'p}{\sin o'o} = \frac{001 \ 11\bar{1}}{111 \ 110} \cdot \frac{111 \ 110}{001 \ 1\bar{1}\bar{1}}.$$

When the values of the known angles are inserted the left-hand side of the equation becomes :

$$\frac{\sin co}{\sin oo'} \cdot \frac{\sin 43^\circ 16'}{\sin 77^\circ 26'}.$$

The right-hand side is to be cross-multiplied by taking the second and third pairs each time, rather than the first and second ; for the latter procedure would make two ciphers  $\frac{0}{0}$  the result in the case of the first fraction, and thus render the final result indeterminate and valueless. Cross-multiplying, therefore, the second and third pairs, we obtain :

$$\begin{array}{r} 001 \ 11\bar{1} \\ \times \quad \times \\ 111 \ 110 \\ \hline 001 \ 11\bar{1} \end{array} = \frac{0 \times 1 - 1 \times 1}{0 \times 0 - 1 \times 1} \cdot \frac{1 \times 0 - \bar{1} \times 1}{1 \times 1 - \bar{1} \times 1}$$

$$\begin{array}{r} 110 \ 111 \\ \times \quad \times \\ 111 \ 110 \\ \hline 0-1 \ 0+1 \end{array} = \frac{0-1}{0-1} \cdot \frac{0+1}{1+1} = \frac{1}{2}.$$

Hence, the whole equation simplifies to :

$$\frac{\sin co}{\sin oo'} = \frac{\sin 77^\circ 26'}{2 \sin 43^\circ 16'}.$$

The right-hand part of the equation works out to a number, and this may be considered as  $\tan \theta$ , in accordance with a familiar trigonometrical device ; that is :

$$(a) \quad \frac{\sin co}{\sin oo'} = \frac{\sin 77^\circ 26'}{2 \sin 43^\circ 16'} = \tan \theta.$$

Working out the value of  $\theta$  with the aid of logarithms :

Log. 2	0.30103	Log. $\sin 77^\circ 26'$	$\bar{1}.98947$
Log. $\sin 43^\circ 16'$	$\bar{1}.83594$	Log. $2 \sin 43^\circ 16'$	$0.13697$
	<u>0.13697</u>		<u><math>\bar{1}.85250</math></u>
			Log. $\tan 35^\circ 27'$

The value of  $\theta$  is thus  $35^\circ 27'$ . The object of considering the numerical value of the right-hand part of the equation as the tangent of an angle is in order that we may convert  $\frac{\sin co}{\sin oo'}$  into a form suitable for logarithmic calculation, and in which the two unknown angles  $co$  and  $oo'$  may be reduced to one unknown by taking advantage of our knowledge of their sum, for this is  $=cp + po' = 120^\circ 42'$ . Such a convenient form is obtained by employing the well-known formula for  $\tan (45^\circ - \theta)$ , namely,  $\frac{1 - \tan \theta}{1 + \tan \theta}$ . For in the equation :

$$(b) \quad \frac{1 - \tan \theta}{1 + \tan \theta} = \tan (45^\circ - \theta)$$

we can substitute for  $\tan \theta$  its equivalent value  $\frac{\sin co}{\sin oo'}$ , taken from equation (a); we then get :

$$(c) \quad \frac{1 - \frac{\sin co}{\sin oo'}}{1 + \frac{\sin co}{\sin oo'}} = \frac{\frac{\sin oo' - \sin co}{\sin oo'}}{\frac{\sin oo' + \sin co}{\sin oo'}} = \frac{\sin oo' - \sin co}{\sin oo' + \sin co} = \tan (45^\circ - \theta).$$

We can now transform the third fraction in (c) into the form of the quotient of the tangent of half the difference by the tangent of half the sum of the two angles, a result well known in trigonometry, and which calls for no proof here. Thus,

$$(d) \quad \frac{\sin oo' - \sin co}{\sin oo' + \sin co} = \frac{\tan \frac{oo' - co}{2}}{\tan \frac{oo' + co}{2}} = \tan (45^\circ - \theta).$$

It now only remains to transpose, thus :

$$(e) \quad \tan \frac{oo' - co}{2} = \tan \frac{oo' + co}{2} \cdot \tan (45^\circ - \theta).$$

The terms on the right-hand side of this final equation (e) are both known, the first being half the known sum of the angles ( $120^\circ 42'$ ), namely,  $60^\circ 21'$ , and ( $45^\circ - \theta$ ) being  $9^\circ 33'$ . Hence, we have

$$\tan \frac{oo' - co}{2} = \tan 60^\circ 21' \cdot \tan 9^\circ 33'.$$

Working this out logarithmically,

$$\begin{array}{rcl} \text{Log. tan } 60^\circ 21' & 0.24471 \\ \text{Log. tan } 9^\circ 33' & \bar{1}.22593 \\ \hline & \bar{1}.47064 = \text{Log. tan } 16^\circ 28', \end{array}$$

we find that half the difference of the two angles is  $16^\circ 28'$ . We now possess, therefore, the knowledge that

$$oo' + co = 120^\circ 42',$$

and

$$oo' - co = 32^\circ 56'.$$

By addition, therefore,

$$2oo' = 153^\circ 38', \text{ from which } oo' = 76^\circ 49';$$

and by subtraction

$$2co = 87^\circ 46', \text{ from which } co = 43^\circ 53'.$$

The remaining angle  $op$  is at once afforded by the difference of the given value of  $cp$  and the value now found for  $co$ , or of the found value of  $oo'$  and the given value of  $po'$ . That is,

$$op = \left\{ \begin{array}{l} cp - co = 77^\circ 26' - 43^\circ 53' \\ \text{or} \\ oo' - po' = 76^\circ 49' - 43^\circ 16' \end{array} \right\} = 33^\circ 33'.$$



Thus the final result of the calculation is that :

$$\begin{aligned} co &= 43^\circ 53', \\ op &= 33^\circ 33'. \end{aligned}$$

It may be interesting to remark that the angles found by actual measurement in this particular case were  $co=43^\circ 51'$  and  $op=33^\circ 30'$ , which affords both a satisfactory proof of the accuracy of the calculations, and an example of the usual degree of agreement between calculated and measured angular values, in such cases as the present, when the degree of reliability of the measured value is not quite so high as in the cases of the more frequently measured angles used as the basis of calculation.

The above example having been worked through from first principles, it may have appeared more complicated than it really is. For we have only to work out in practice the value of  $\tan \theta$  in equation (a), and then at once to set down the equation (e) and work out from it the value of the difference of the two angles required ; this, by addition to and subtraction from the known sum of the two angles, at once enables us to find the two required angles, either of which defines the position in question of the fourth pole in the zone.

When one of the angles is a right angle, the formula becomes simplified to the ratio of two tangents. For example, in the case of the same crystal of monoclinic ammonium selenate the question arose of finding the magnitude of the angle  $ap'$  in the zone  $[ap'pb]$  shown in the stereographic projection, Fig. 42, and diagrammatically to represent the conditions in Fig. 45. The angle  $ap$  had been thoroughly well measured (36 times) and shown to be  $59^\circ 38'$ , but  $ap'$  had only been measurable 4 times, and so it was desired to calculate its value for the sake of verification, from the more certain value of  $ap$ . The angle  $ab$  was a right angle, the plane  $b$  being the symmetry plane and  $a$  one of the fundamental faces, that is, chosen as an axial plane, lying in the zone perpendicular to the symmetry plane.

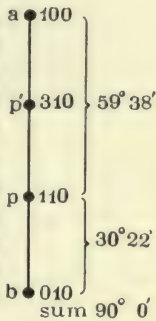


FIG. 45.

Writing down the anharmonic ratio, starting as usual from the two ends, we get :

$$\frac{\sin ap'}{\sin ap} \cdot \frac{\sin bp}{\sin bp'} = \frac{ap'}{ap} \cdot \frac{bp}{bp'}.$$

Putting in the values of the indices on the right-hand side, and the values of the known angles on the left-hand side, and instead of  $\sin bp$  ( $bp=30^\circ 22'$ ) and  $\sin bp'$  substituting their equivalents (being a right-angled triangle)  $\cos ap$  and  $\cos ap'$ , that is, the cosines of their complements, we obtain :

$$\frac{\sin ap'}{\sin 59^\circ 38'} \cdot \frac{\cos 59^\circ 38'}{\cos ap'} = \frac{100}{110} \cdot \frac{010}{310}.$$

Cross-multiplying the first two pairs of indices in each case, as the second and third pairs would not yield a finite result, we obtain :

$$\tan ap' \cdot \cot 59^\circ 38' = \frac{1}{1} \cdot \frac{1}{3}$$

or

$$\tan ap' \cdot \cot 59^\circ 38' = \frac{1}{3}.$$

Transposing, and replacing  $\frac{1}{\cot 59^\circ 38'}$  by  $\tan 59^\circ 38'$ , we obtain the simple expression:

$$\tan ap' = \frac{1}{3} \tan 59^\circ 38'.$$

Working this out :

$$\text{Log. } \tan 59^\circ 38' 0.23217$$

$$\text{Log. } 3 \ 0.47712$$

$$\text{Log. } \tan ap' \ 1.75505 = \text{Log. } \tan 29^\circ 38'$$

we find that :

$$ap' = 29^\circ 38'.$$

The value of the angle obtained by taking the mean of the four measurements was  $29^\circ 36'$ , the two values thus satisfactorily confirming one another.

This last is also an excellent example of the converse use of the anharmonic ratio of four poles in a zone for determining the symbol of a face. For there was some doubt when the crystals of ammonium selenate were being investigated as to whether the proper symbol of the face  $p'$  were (210) or (310). For the crystals are not isomorphous with those of orthorhombic ammonium and potassium sulphates, but belong to the monoclinic system, and are thus quite different from the latter salts, so that we cannot compare the indices. Now, if the symbol be (310), the angle is, as we have seen,  $29^\circ 38'$ . But if it were (210), and we substituted those indices for (310) on the right-hand side of the expression for the anharmonic ratio, we should get :

$$\tan ap' = \frac{1}{2} \tan 59^\circ 38',$$

and  $ap'$  would work out to be  $40^\circ 29'$ . Now, the position of the face was found by direct measurement four times, and although there was not such certainty about the mean result as regards the last minute (it has been shown to differ  $2'$  from the calculated value) as in the case of the basal angle  $ap$ , which had been measured as often as thirty-six times on different crystals and on different parts of the same crystal (the angle being repeated four times on going round the zone), still it was absolutely certain that the true value was quite near to  $29\frac{1}{2}^\circ$  and consequently very far removed from  $40\frac{1}{2}^\circ$ . Hence the indices were certainly (310) and not (210).

So much space has been devoted to this principle of four poles in a zone because of its unique practical importance. For with its aid, and that of the principles which have been elucidated for finding the indices of faces by zonal intersections, together with such of the ordinary formulæ for the solution of spherical triangles as are suitable for logarithmic calculation (these triangles being shown directly on the stereographic projection), the whole of the calculations of practical morphological crystallography can be carried out. It is essential, therefore, that the few principles discussed in this chapter should be thoroughly mastered, for when that desirable consummation is achieved all difficulty with the subject will disappear.

The invaluable nature of the stereographic projection will have impressed itself more and more during the elucidation of these principles. For it not only furnishes in one complete diagram a review of the symmetry of the crystal, but also indicates, by showing at once all the possible triangles formed by the numerous intersecting zone circles, how we can proceed to make the required calculations. That is, it enables us to see at a glance when to employ the anharmonic ratio for the determination of the position of any fourth pole in a zone, and when to determine the angle between any pair of faces whatsoever with the aid of one or other (and which) of the usual formulæ of spherical trigonometry just referred to, the more practically convenient of which will be given at the commencement of the next chapter. It affords, moreover, as will subsequently be shown, the diagram for the calculation of the relative lengths of the crystal axes and the axial angles, in the cases where these latter are not  $90^\circ$ . It is advisable, therefore, that this chapter should close with a concise account of the principles which govern the construction and use of the stereographic projection, including one or two important propositions not already elucidated during the measurement of the typical crystal of potassium sulphate.

### **The Stereographic Projection of the Arrangement of Crystal Faces.**

—The elementary rules concerning this invaluable mode of representing graphically the symmetry of a crystal have already been elicited in Chapter IV., during the process of measuring the typical crystal of potassium sulphate. It is necessary now, however, after having thus fully considered the subject of indices and that of zonal relationships, to summarise them, and to extend them so as to meet the cases of crystals in general.

The following are the three chief principles and facts on which the practical application of the stereographic projection depends.

(1) Every circle on the sphere appears in the projection as a circle (the primitive circle) or circular arc, or as a diameter of the primitive circle; and if the circle in question be a great circle (the section of a sphere by a plane passing through the centre of the sphere), it appears in the projection as a diameter, or as a circular arc which cuts the primitive circle at the ends of a diameter. Moreover, all zone circles perpendicular to the primitive circle have their poles on the latter, and appear in the projection as diameters.

(2) The pole of a zone circle is the projection of that point on the sphere which is situated  $90^\circ$  from all points on the zone circle; in other words, it is the pole of the zone plane, or of a face at right angles to the faces of the zone in the event of such a face being possible.

(3) If the poles of any two faces belonging to a zone be joined to the pole of the zone circle, and if the two straight lines thus obtained be produced until they cut the primitive circle, then the arc thus cut off and enclosed on the primitive circle will be equal to the angle between the faces.

The following practical rules for the application of these principles will be found to cover the cases of crystals in general, including the more difficult ones of triclinic or asymmetric crystals.





point. Now, as A is the pole of the zone BQB', if we draw the straight line joining A and Q and produce it to R on the primitive circle, and if we then mark off the point S at  $90^\circ$  on that circle, to the left of R, and join AS, then the projection of the desired pole will be at T, where AS cuts the diameter BQOB'. For QT, when projected on to the primitive circle from the pole A of the zone circle represented in the projection by the diameter BQTB', on which zone circle the required pole must lie, projects into an angle of  $90^\circ$  on the primitive circle, by construction, so that, by principle (3) T is the projection of a point situated  $90^\circ$  from Q, as desired.

It is interesting to observe that as the radius of the zone circle becomes greater, and the curve consequently becomes flatter, the pole recedes along the perpendicular diameter and approaches the primitive circle, as instanced by the pole P of the zone *bqcq'b* in Fig. 48, until, in the limiting case, the zone circle also becomes a diameter and the pole then lies actually on the primitive circle itself, at the extremity of the perpendicular diameter, in accordance with the last sentence of principle (1).

It will generally happen, except in the few cases met with of entire absence of symmetry, or of all but centro-symmetry, in the crystals of a substance, that the stereographic projection can be completed without having actually to construct (from a couple of angular measurements only, defining the position of a face not on the primitive zone with respect to faces on that zone) a zone circle which is not a diameter in the projection. The presence of symmetry, as in the typical case of potassium sulphate considered in Chapter IV., generally ensures that, after having drawn in the poles on the primitive circle, representing the faces on the principal zone, and having joined the poles of opposite parallel faces by diameters, the poles of most of the remaining faces will lie on those diameters; and even the more complicated, rare, or subsidiary faces will lie on such curves, representing other zones, as can be readily drawn in; for three points will already have been found on them, namely, two on the primitive circle at the ends of a diameter, and the third on another diameter. It is only a matter of finding the centre of the curve and actually constructing it, which can be done either by trial, or by the usual procedure of plane geometry as given on the last page.

Having thus constructed the zone circle and found its pole, it only remains to apply rule (3) in order to be able to find the positions of the poles of the faces of the zone, namely, by setting off the measured angles along the primitive circle and on the further side of it from the pole of the zone circle, starting from one of the two facial poles common to the primitive and zone circles, and joining the points thus obtained on that circle to the pole of the zone circle; the points of intersection of those straight lines with the zone circle will be the required poles, exactly as described on page 66, Chapter IV., for potassium sulphate and graphically shown in Fig. 37.

The procedure is not quite so simple, however, in the absence of symmetry, or where there is merely centro-symmetry, as in the crystals

of the triclinic system. In such a case we can only proceed as already indicated as far as choosing the best-developed zone for that which is to be considered as perpendicular to the plane of projection, and drawing in the primitive circle with its poles at the angular distances measured between the normals to the faces. An example is given in Fig. 48, which represents the stereographic projection of a typical triclinic substance, methyl triphenylpyrrholone.

One of the actual crystals of this substance investigated by the author is shown in Fig. 47, drawn to scale by the conventional method to be described in Chapter XXV. The construction of the triclinic axes corresponding to the crystal is fully described in that chapter, and illustrated

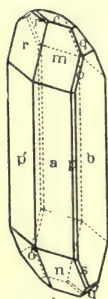


FIG. 47.—Crystal of Methyl Triphenylpyrrholone.

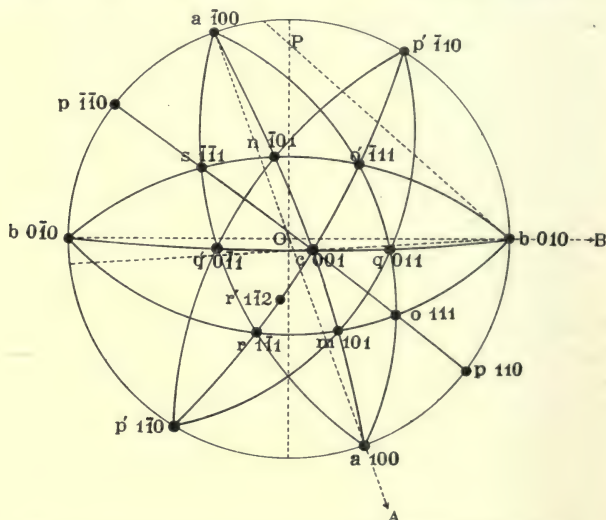


FIG. 48.—Stereographic Projection of Methyl Triphenylpyrrholone.

in Fig. 358. The basal plane  $c = (001)$  is now no longer perpendicular to this zone of faces chosen to afford the primitive circle, and parallel to the plane of projection, as was the case with the orthorhombic crystal of potassium sulphate, so it cannot be represented by the usual dot at the centre of the primitive circle. We know from the measurements, however, the inclination of the important face  $c$ , which we choose as basal plane  $(001)$ , to the two other primary faces  $a = (100)$  and  $b = (010)$ . If we let  $\theta$  and  $\phi$  represent these two angles  $a : c = (100) : (001)$  and  $b : c = (010) : (001)$  respectively, we can then make the following simple construction and calculation in order to arrive at the position of the pole of the basal plane  $c$  on the projection. We produce the diameters (dotted in Fig. 48)  $aa$  and  $bb$ , the former forwards and the latter to the right, and then  $r$  being the radius of the primitive circle, we take lengths  $QA$  and  $OB$  along them from the centre  $O$  such that :

$$OA = \frac{r}{\cos \theta}, \text{ and } OB = \frac{r}{\cos \phi}.$$



Then from each of the points A and B we draw a circular arc the radius of which is, in the respective cases :

$$Ac = r \tan \theta, \text{ and } Bc = r \tan \phi.$$

These two arcs will intersect each other within the primitive circle at the pole *c* of the basal plane (001). We have then three points on each of the zones *aca* and *bcb*, and can therefore at once construct the two zone circles.

In the case of methyl triphenylpyrrolone, the radius *r* of the primitive circle in the original drawing, of which Fig. 48 is an approximate half-size reproduction, was 55 millimetres;  $\theta$ , the angle *ac* as measured on the crystal, was  $82^\circ 2'$ , and  $\phi$ , the measured angle *bc*, was  $77^\circ 24'$ . The calculations for OA and OB, and for Ac and Bc, were then as under :

Log. $r$	1.74036	Log. $r$	1.74036		
Log. $\cos \theta$	1.14175	Log. $\cos \phi$	1.33874		
<hr/>					
Log. OA	2.59861	OA = 396.8 mm.	Log. OB	2.40162	OB = 252.1 mm.
Log. $r$	1.74036		Log. $r$	1.74036	
Log. $\tan \theta$	0.85403		Log. $\tan \phi$	0.65067	
<hr/>					
Log. Ac	2.59439	Ac = 393.0 mm.	Log. Bc	2.39103	Bc = 246.1 mm.

As the points A and B are thus respectively about seven and five times as far from the centre O as the points *a* and *b*, they are not shown in Fig. 48, the arrows indicating their directions. They were, of course, actually found on the large sheet of cardboard on which the original drawing was made, and employed as the centres for the arcs Ac and Bc, but for reproduction purposes it was necessary to eliminate these two very long straggling construction lines. In the case of copper sulphate they were not nearly so long, so they are shown in the Fig. 228 representing the stereographic projection of that substance in Chapter XIX.

The poles of the remaining faces can be found in a similar manner if necessary, but usually it is only necessary to find *c*, or, in the absence of a basal plane, some one other pole. Occasionally, as in the case of copper sulphate crystals, described in Chapter XIX., the angle *ac* or *bc* (in the case of copper sulphate it is *bc*) is slightly more than  $90^\circ$ , and it is then more convenient to choose another face than *c*, the angles of which with *a* and *b* are less than  $90^\circ$ , for convenience of calculation by use of the formulæ just given. The face *g* = (011) is convenient in the case of copper sulphate. Other pairs of poles of parallel faces on the primitive circle will form zones with the pole just found, and the construction of these two or three zone circles enables us at once to determine the positions along them, by the method already described, of the poles of the other faces belonging to these zones, when, as is likely, others are present. Having thus found the positions of quite a number of facial poles, other zones will be apparent passing through fresh combinations of them, and their zone circles can be similarly readily constructed. Consequently the whole stereographic projection can as a rule be constructed without having recourse to calculation for the position of more than one pole, and, as we have already seen, if symmetry be developed even this one calculation can generally be dispensed with.

It will thus be apparent in how emphatic a manner the stereographic projection brings out the important fact that the faces of crystals are arranged in zones, and how clearly it renders apparent any symmetry that may exist, as regards both the disposition of the individual faces and that of the zones into which they fall.

**Aids to the Construction of Stereographic Projections; Wulff and Fedorov's Ruler for Circles of large Radius; Hutchinson's Stereographic Protractor and Stereographic Net.**—The drawing of a circular arc of large radius, that is, of a flat curve, in the cases of great circles on a stereographic projection which are nearly straight lines, is often a somewhat difficult matter with even a large pair of compasses, and the exact attainment of the required accuracy with which the arc passes through the ends of the diameter on the primitive circle, where diameter, primitive circle, and the large arc should intersect, as well as through any other poles already found, is not easy. For such cases a **curved ruler**, of which the curvature is capable of variation while preserving the circular nature of the arc, was suggested by both Wulff and Fedorov, and is now constructed, in accordance with the designs of

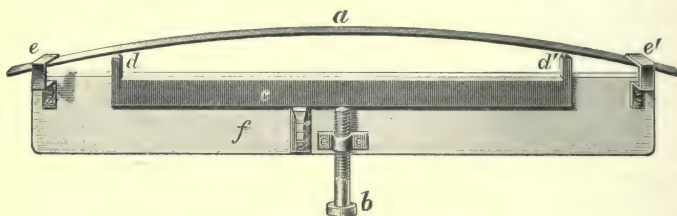


FIG. 49.—Fedorov's Ruler for Circular Arcs.

the latter, by Fuess of Berlin. It is shown in Fig. 49. It consists essentially of a strip of steel *a*, sufficiently thin to be readily bent into a bow by means of a screw *b*, applied like an arrow except for two important differences. Firstly, it is applied to the bow itself and not to the equivalent of the string, which is a rigid bar *c* moved parallel to itself by means of the screw; and secondly, the force is not applied in one place at the middle of the bow but at two places *d* and *d'* equidistant and not very far from each end. The rigid bar terminates at these positions in a pair of wedges or slightly rounded knife-edges parallel to the surface of the curved strip, which is slightly oblique in order to afford greater facility for the use of the ruling pen; the wedges push the strip circularly outwards so that the maximum movement is at the centre, while it is prevented from moving outwards at all at the ends, but is left free to move in the direction of its length, by means of and between a pair of guides *ee'*, which act as the fulcrum supports; it can readily adjust itself, therefore, to any circular arc which it is constrained to form by the action of the screw and the pressure of the wedges which the latter actuates. The mother-nut of the screw is fixed rigidly to a basal plate *f*, by which the apparatus rests on the drawing in the position required for the construction of the circular arc.

The steel strip acts in this instrument like the bar supported on two knife-edges near its ends, in the well-known elasticity experiment, and which is loaded above at two points symmetrically situated with respect to the two supports and within the latter nearer to the centre. The curve produced by such a bar is nearly a circular arc, and in the case of the steel strip the approximation to a circle, when the screw is only used to the extent required to produce fairly flat curves for which the compasses are not readily available, is so close that the difference is not perceptible on the scale of the drawing. A full discussion of the theory of the instrument will be found in Fedorov's memoir.<sup>1</sup>

The **protractor** devised by Dr. Hutchinson to facilitate the construction of stereographic projections is constructed in boxwood by Harling (47 Finsbury Pavement, London). It is shown in Fig. 50, and its method of use in Fig. 51. It is intended for a projection the primitive circle of which is of  $2\frac{1}{2}$  inches radius. It is about a foot long and is exactly 2.5 inches wide. A circle of 5 inches diameter is very convenient in size for a stereographic projection intended for publication, by photo-process reproduction on a reduced scale. The necessary circles to represent the various zones on a stereographic projection of such a size may be readily drawn with the large compasses of any good box of mathematical instruments, or, when the radius is very large, by means of the Wulff-Fedorov circular ruler just described.

The protractor has a zero line, OZ in Fig. 51, drawn across it at right angles to its length, and at a distance from one end rather greater than its width. Taking Z as centre, where the zero line intersects one of the longer edges, the opposite long edge ST is graduated by means of a circular dividing engine. The portion of the scale from O to T is divided into degrees, just like an ordinary protractor, and every tenth division is numbered in duplicate, the numbers running both ways, as shown in the figures. The divisions along OS are the same as those from  $0^\circ$  to  $45^\circ$  along OT, but are numbered so that each division represents  $2^\circ$  instead of  $1^\circ$ . The finer divisions are omitted in the figures for the sake of clearness, but they are very clearly engraved on the protractor itself.

The distance from O of any division lying between O and T is obviously numerically equal to the tangent of the corresponding angle, read on the upper row of numbers, when measured with a scale for which the radius of the primitive circle is taken as the unit. Such a scale is provided on the back of the protractor, and in order that the tangent may be expressed as usual in decimals, its numbered unit is a quarter of an inch, one tenth of 2.5 inches; each numbered unit is further subdivided into tenths, so that the actual engraved unit-mark of the scale is one-fortieth of an inch.

The distance from O of any division along OS is numerically equal to the tangent of half the angle as read on the lower row of numbers, and the divisions themselves correspond to degrees stereographically projected on a diameter. This enables us at once to perform the following operations.

(1) The position of a facial pole P, situated on any diameter and the angular distance of which from the centre of the primitive circle (or its complement, from the primitive circle itself) is known, may at once

<sup>1</sup> *Zeitschr. für Kryst.*, 1893, 21, 618.





carried by the other leg of the compass passes through P in constructing the circular arc BPZ. This construction depends on the fact that if  $r$  be the radius of the primitive circle and  $\theta$  the angle OP, then  $pP$  the radius of any great circle BPZ is numerically equal to  $r \operatorname{cosec} \theta$ .

(3) The pole  $P'$  of a great circle such as BPZ may also be easily found with the protractor still in the same position. We take the reading of P on the scale OS, using the upper numbers, divide this reading by two, and find on the upper number scale of OT the reading corresponding, which will be that of the required pole  $P'$  of the great circle BPZ. Thus in Fig. 51 the upper row reading for P along OS is  $50^\circ$ , half this is  $25^\circ$ , and at  $25^\circ$  along OT, using the upper row of numbers, we have the position of  $P'$ . The proof of this is, that the stereographic position of P on OS being  $40^\circ$  and that of  $P'$  being (stereographically also)  $25^\circ \times 2$ , or  $50^\circ$ , the sum of the two stereographic positions  $40^\circ + 50^\circ$  is  $= 90^\circ$ , and by definition the pole of a great circle is  $90^\circ$  removed from all points upon it. (It will be remembered that a "great circle" is the section of a sphere by a plane which passes through the centre of the sphere, a "small circle" being a section by any other plane.)

A very valuable property of the stereographic projection is its angular truth, for the angles between great circles on the sphere are preserved in the projection. We can, therefore, determine the angles between zones which intersect at a certain point by drawing tangents to the zone circles at the point where they meet, and measuring the angle between these tangents. This, of course, can readily be done by using the ordinary protractor scale along OT.

It will often be required, also, to measure the angle between two crystal faces of which the projected positions have been found. This requires the construction of the great circle passing through the points and the determination of the pole of this great circle. This can always be done by means of the protractor, using operations (2) and (3), and making use of other information which will be available to enable the terminations of the great circular arc on the primitive circle to be fixed, that is, the ends of a diameter which are also points on the great circle in question.

Many other problems can also be solved with equal facility with the aid of this stereographic protractor, such, for instance, as the construction of a small circle, of given angular radius, round any point either on or within the primitive circle, and an account of them will be found in the original memoir of Dr. Hutchinson.<sup>1</sup>

The last of the problems above referred to, and many others relating to stereographic projection, may be more rapidly solved by means of a **stereographic net**. The use of such nets has been pointed out by Fedorov, Wulff, Penfield, and other investigators, and a very convenient one has been prepared by Dr. Hutchinson for a primitive circle of 2.5 inches radius, corresponding to the stereographic protractor. It is shown in Fig. 52. The great circles and small circles

<sup>1</sup> *Min. Mag.*, 1908, 15, 93-112.

constructed on this net are only  $2^\circ$  apart, so that the positions of poles on the projection can be found with great precision. A copy of the net on tracing-paper is exceedingly useful, as it enables the positions found on it to be directly pricked through on to the drawing which is being made on Bristol board for the purposes of reproduction, or if publication be not intended, on to the drawing which is being made on drawing paper or in the note-book, without injuring the original net, a new tracing being taken whenever the one in use becomes spoilt with frequent use. If reproduction be intended, another useful method of procedure is to make a preliminary drawing on tracing-paper, and to place it above the net (either the one in the book or the loose one on tracing-paper), when the particular problem can readily be solved. For instance, in the case of the second one above referred to, the measurement of the angle between two points, the tracing-paper drawing is placed over the net so that the two centres are coincident, and with a needle stuck through them; the angular distance between the two points in question may then be determined by rotating the drawing above the net until the two points lie along the same great circle, or evenly between two adjacent ones. The angular distance between the points may then be read off immediately by means of the small circles. The problem can also be solved without the use of a tracing by means of a three-legged compass; two of its legs are arranged so as to be placed on the two points when the third is on the centre of the primitive circle; the compass points are then transferred to the net, the same point being placed on the centre, and the compass is rotated about this leg until the other two legs lie on the same great circle.

An exceedingly interesting account of the history of the stereographic projection will be found in Dr. Hutchinson's memoir, going

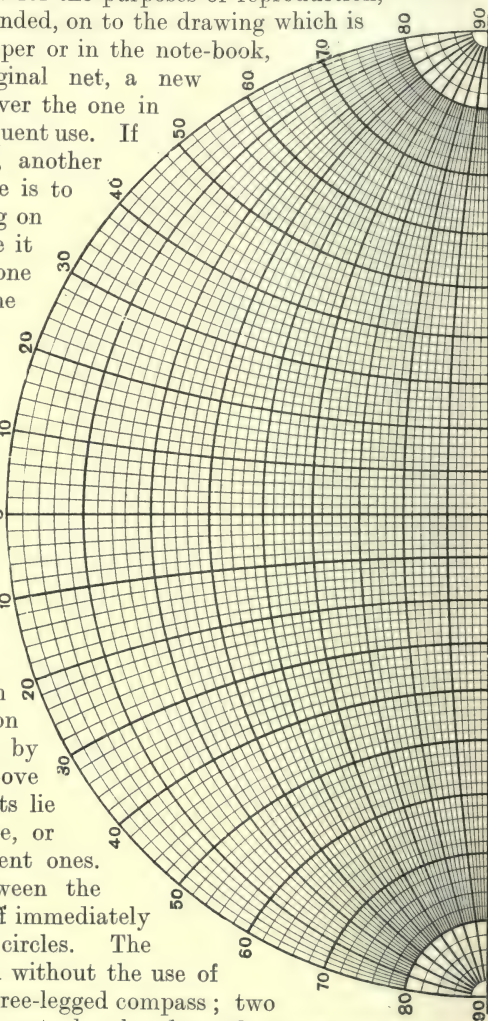


Fig. 52.—Hutchinson's Stereographic Net.



back to Ptolemy, and to his greater predecessor Hipparchus, whose writings concerning the projection are unfortunately lost to us, except what we know through the preserved works of Ptolemy. It has already been stated in Chapter IV. that its use in crystallography was first pointed out by Neumann, in his *Beiträge zur Krystallonomie*, dated 1823. Its use in England was taken up by Professor W. H. Miller of Cambridge, and forms the basis of his *Treatise on Crystallography* published in 1839 already referred to in the last chapter, as the graphical expression of the system of facial indices which he introduced, and which has ever since borne his name and is now practically universally employed. Des Cloizeaux employed it later in his *Manuel de minéralogie*, the first volume of which was published in 1862. It has been much further developed, however, of late years by Fedorov<sup>1</sup> and Wulff,<sup>2</sup> who both published stereographic nets for a primitive circle of 10 centimetres radius, and indicated the use of the triangular compass with them. Benno Hecht also published a net for a circle of 5 c.m. radius in his *Anleitung zur Krystallberechnung* dated 1893, and Sommerfeldt<sup>3</sup> has since extended this beyond the boundary of the primitive circle. V. Goldschmidt<sup>4</sup> has also discussed the stereographic projection as regards its use for dealing with the data obtained by the use of the two-circle goniometer.

The name of Penfield stands out predominately, however, as regards modern work on the stereographic projection. In a series of papers to the *American Journal of Science*, beginning with two in 1901 (ser. 4, vol. xi. pages 1 and 115), and including two important ones in vols. xiii. and xiv., Penfield has given a most exhaustive treatment of the subject, and published stereographic nets printed on transparent celluloid. Penfield also introduced sheets of paper on which are printed a circle of 7 c.m. radius divided into degrees, together with four scales; the first two give the radii of great and small circles respectively, the third is a scale of stereographically projected degrees, and the fourth is one the unit of which is the one-hundredth part of the radius.

All these constructions of Penfield's can now be carried out with the stereographic protractor of Hutchinson, and if the latter be constructed for a 7 c.m. radius it will be found more convenient with Penfield's circle than the four scales given by Penfield himself. But, as already stated, the net of 2.5 inches (6.3 c.m.) radius given by Hutchinson is one of a particularly convenient size, and the 2.5 inch protractor and net together afford the best aids to the construction of stereographic projections which have yet been described.

<sup>1</sup> *Zeitschr. für Kryst.*, 1893, 21, 617, and 1903, 37, 138.

<sup>2</sup> *Ibid.*, 1893, 21, 253, and 1902, 36, 14.

<sup>3</sup> *Ibid.*, 1906, 41, 164.

<sup>4</sup> *Ibid.*, 1899, 30, 260.

## CHAPTER VII

### THE FEW INDISPENSABLE FORMULÆ REQUIRED FOR THE CALCULATION OF CRYSTAL ANGLES AND ELEMENTS

HAVING in the last chapter elucidated the main lines on which the general structure of crystals is conceived, and brought into prominence the important principle of rationality, as regards both intercepts and indices, and also developed the interesting laws regarding the arrangement of faces in zones, we are now in a position to work out to a logical conclusion the typical experimental results obtained with the orthorhombic crystal of potassium sulphate the goniometry of which was described in Chapter IV., and we shall proceed to do so in the next chapter. Before so doing, the chief formulæ employed in the calculation of crystal angles from the necessary given data—one, two, three, or five thoroughly well measured basal angles, according as the symmetry is tetragonal or hexagonal, orthorhombic, monoclinic, or triclinic respectively, as will be fully proved and explained in subsequent chapters—and in the derivation of the crystal elements, will be dealt with in this chapter and the task of Chapter VIII. thereby rendered simple and straightforward.

Students of crystallography have so frequently been discouraged by the formidable array of mathematical formulæ set out in books on the subject, particularly with respect to the calculation of crystal angles and elements, that it is one of the author's chief aims to dispel the cloud of misconception which has arisen as to the difficulty of the science. **The only mathematical endowment required is the ability to employ the ordinary formulæ for the solution of spherical triangles, that is, an elementary knowledge of plane trigonometry and the ability thereby conferred to use the very similar formulæ of spherical trigonometry.** An advanced study of the latter subject is unnecessary, although, of course, the writer would be the last person to deny that a superior knowledge of higher mathematics is an equipment of the utmost value to an investigator in this branch of science. It will, however, be the author's special task to make the calculation of goniometrical results simple and clear. The few essential formulæ will first be stated in this chapter, and then with this endowment a typical series of crystals of all the degrees of symmetry will be worked out from first principles in subsequent chapters, beginning with the calculation of the results

for potassium sulphate, as the first of these typical crystals, in a general manner which should always be employed with regard to every crystal investigated.

**Chief Formulæ used in Calculation of Crystal Angles from the Basal Angles.**—The few fundamental formulæ in question, which are of constant use in all such calculations, will now be stated.

(1) The first of these is the all-important **anharmonic ratio of four poles in a zone**, which has been fully set out and explained in the last chapter.

(2) Next come **Napier's rules for the solution of right-angled spherical triangles**. A spherical triangle has six parts or elements, namely, three sides and three angles, the sides as well as the angles being, unlike plane triangles, circular arcs and therefore stated in angular measure just like the angles. In a right-angled spherical triangle one of the six parts is known to be  $90^\circ$ , and only the other five parts appear in Napier's rules.

If we draw a vertical line AB, and from its centre draw on the right hand another line at right angles to it, and on the left-hand side two lines radiating from the same central point on AB, at about  $60^\circ$  to each other and to AB, as shown in Fig. 53, then the five parts of a right-angled spherical triangle other than the right angle may be considered as represented diagrammatically by the five angles or compartments of the figure. The sixth part, the right angle itself, is supposed to be represented by the horizontal line to the right of AB, and the compartments of the figure above and below it represent the two parts of the spherical triangle adjoining the right angle; these two parts are, of course, not right angles as actually shown in the figure, the line AB being drawn as a vertical straight one for the express purpose of dividing the five parts into two sets, one set consisting of the two parts adjoining the right angle and the other set consisting of the other three parts, for a reason which will be apparent directly. In some text-books the five radiating lines separating the five parts are drawn at equal angular distances, but the relation which it is desirable to emphasise is not so well brought out on such a figure. The right angle of a spherical triangle may, it must be remembered, be either a side or an angle, for the reason already mentioned that the sides are, equally with the angles, measured in degrees and minutes. Hence, in giving a general statement of Napier's rules it will be clearer not to letter the parts, as we should do in the case of any specific triangle; for the right angle which disappears may be any one of the six parts  $a, b, c$  (the sides),  $A, B, C$  (the angles). Instead, we shall number them I to V, I being either of the two parts (angle or side) adjoining the right angle and V being the other part adjoining the right angle. Then we place the other three parts in the left-hand compartments of the diagram, in the order in which we meet with them in going round the triangle. Thus, if we elect to start by

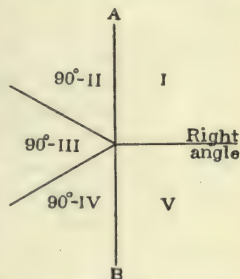


FIG. 53.



placing the part I above the rectangular horizontal line, that is, in the top right-hand compartment, II will come in the top left-hand compartment, III in the middle compartment on the left-hand side of AB, IV in the lower compartment of the same side, and V finally in the lower right-hand compartment. The horizontal line itself, representing the sixth  $90^\circ$  part, does not enter into the formulæ.

**Napier's rules** are then as follows :

$$\text{The sine of the middle part} = \begin{cases} \text{The product of the tangents of the} \\ \text{adjacent parts, or} \\ \text{The product of the cosines of the} \\ \text{opposite parts.} \end{cases}$$

Provided : (a) That by "the middle part" we mean any one of the five parts which it may be convenient to choose as such either because it is the part the value of which it is desired to calculate, the two adjacent or the two opposite parts being known, or because it is one of the two known parts, the other of which together with the part required form the two opposite or adjacent parts ; that all parts are equally eligible for such choice, whichever side of the line AB they may be ; that by "the adjacent parts" we mean the two parts lying next to and on each side of the part chosen as middle part ; and that by "the opposite parts" we mean the two parts opposite to the part chosen as middle part. (b) That if any part—be it the middle part, an adjacent part, or an opposite part—lie to the left of the line AB, the angle " $90^\circ - \theta$ " the angular value of the part" shall be understood, instead of the angular value of the part itself. Now, as  $\sin (90^\circ - \theta) = \cos \theta$ ,  $\cos (90^\circ - \theta) = \sin \theta$ , and  $\tan (90^\circ - \theta) = \cot \theta$ , this simply means that the sine of the middle part becomes the cosine of that part when the particular compartment in which the part occurs lies to the left of AB, that the tangent of an adjacent part becomes the cotangent of that part when it lies in a compartment to the left of AB, and that the cosine of an opposite part similarly becomes the sine of that part when it lies left of AB. The reason for making the line of division AB prominent by making it vertical, and the left side at once visibly apparent, will now be appreciated.

When once these conditions have been learnt, Napier's rules will be found to render the solution of the numerous right-angled triangles met with in the calculation of crystal angles a matter of the utmost simplicity, and the method is eminently suitable for ready logarithmic calculation. Numerous examples will be worked out in the next, and later chapters.

(3) When right-angled triangles are not available we have to make use of the ordinary **formulæ for the solution of any required part of any oblique-angled spherical triangle**. If the three sides be  $a$ ,  $b$ ,  $c$ , and the three angles A, B, C, of which A is opposite to the side  $a$ , B opposite  $b$ , and C opposite  $c$ , then when any three of the six parts are known we can always find the other three by the usual formulæ of spherical trigonometry. In lettering the sides and angles it is convenient that  $a$  should be a greater side than  $b$ , and consequently that the angle A should be larger than B, so that  $a - b$  and  $A - B$  may be positive and

not negative, as these expressions occur in the formulæ given below under (c).

In every case only such formulæ should be chosen as are adapted to logarithmic calculation. The chief and most useful of these will now be enumerated.

(a) The first series of formulæ of practical use are those for the calculation of the three angles A, B, C, having given the three sides  $a, b, c$ . These are as follows, when  $s$  = half the sum of the sides :

$$\sin^2 \frac{A}{2} = \frac{\sin(s-b) \sin(s-c)}{\sin b \sin c},$$

$$\sin^2 \frac{B}{2} = \frac{\sin(s-a) \sin(s-c)}{\sin a \sin c},$$

$$\sin^2 \frac{C}{2} = \frac{\sin(s-a) \sin(s-b)}{\sin a \sin b}.$$

These formulæ are very easy to remember, for in each case the square of the sine of half the angle to be calculated is equal to an expression which is of similar type in all three cases, in which besides  $s$  the sides adjacent to the angle under calculation alone occur, and the side opposite to the angle in question does not occur. That is, if the angle A, for instance, is being calculated, only  $b$  and  $c$  appear in addition to  $s$  on the right-hand side; in the case of B, only  $a$  and  $c$ ; and in the case of C, only  $a$  and  $b$ .

(b) To find the third side, which we may call  $c$ , knowing two sides,  $a$  and  $b$ , and the included angle, C.

We assume :  $\tan \theta = \tan b \cos C$ .

Then :  $\cos c = \frac{\cos b \cos(a - \theta)}{\cos \theta}.$

Both these are very short calculations suitable for the use of logarithms.

(c) To find the two sides ( $a$  and  $b$ ), given the two angles (A and B) and the included side  $c$ .

We first calculate  $a+b$  and  $a-b$  from the formulæ :

$$\tan \frac{1}{2}(a+b) = \frac{\cos \frac{1}{2}(A-B)}{\cos \frac{1}{2}(A+B)} \tan \frac{1}{2}c,$$

$$\tan \frac{1}{2}(a-b) = \frac{\sin \frac{1}{2}(A-B)}{\sin \frac{1}{2}(A+B)} \tan \frac{1}{2}c.$$

By addition of  $a+b$  to  $a-b$  we obtain  $2a$ , and finally its half  $a$ . Similarly, by subtracting  $a-b$  from  $a+b$  we obtain  $2b$ , and hence  $b$ .

It will usually be found that the formulæ which have now been enumerated in this chapter are all that are required for the calculation of the whole of the interfacial angles and crystal elements for all crystals up to and including those of the monoclinic system; in the case of this

latter system, from the three best measured angles as basis of calculation. Indeed, in the cases of crystals of higher symmetry, including the orthorhombic, the formulæ for four poles in a zone and Napier's rules generally suffice; only two basal angles are required in cases of orthorhombic symmetry, and these are further reduced to one basal angle in the cases of hexagonal and tetragonal crystals. In the rarer cases of triclinic crystals the formulæ of sections (1) and (3) are chiefly required, and five basal angles must be known, belonging to at least two different triangles, the three sides of the fundamental triangle being conveniently three of the five known angles, for treatment by formulæ (a) of section (3). That is to say, it is convenient to have measured at the outset the three sides  $a$ ,  $b$ ,  $c$  of the fundamental triangle, as a basis for all the calculations; for they are the three angles between the fundamental faces of the crystal parallel to the three axial planes, and the three angles  $A$ ,  $B$ ,  $C$  which can be calculated from them by formulæ (a) of section (3) will be the elementary axial angles  $\alpha$ ,  $\beta$ ,  $\gamma$  (see Fig. 54), as will be shown in the next section of this chapter when we come to consider the mode of calculating the crystal elements. Having commenced by making these fundamental calculations of  $\alpha$ ,  $\beta$ ,  $\gamma$  with the aid of formulæ (a), we shall be able, with the further aid of the other two basal angles, to calculate not only the axial ratios, but also, by stepping from one triangle to another of the stereographic projection in such order as always to find three known parts from which to calculate the other three, the whole of the interfacial angles of the crystal. We can thus find, even in the most difficult case, the "general" case of a triclinic crystal, the value of every arc between every pair of poles on the stereographic projection. Occasionally in the case of triclinic crystals, other of the well-known formulæ for the solution of oblique-angled spherical triangles may be required than are given in section (3), but when such rarer cases occur it will be easy to obtain the formulæ from any standard text-book of spherical trigonometry. In Chapter XIX. a practical example of a fairly complex triclinic crystal will be worked through in detail.

**General Mode of Calculation of the Crystal Elements.**—Fig. 54 represents the upper-right-front octant of the stereographic projection of a triclinic crystal,<sup>1</sup> the most general case. The **axial angles**  $\alpha$ ,  $\beta$ ,  $\gamma$  have the situations shown in the figure; for the arc  $ac$  represents the edge between the faces  $a=(100)$  and  $c=(001)$ , the arc  $ab$  represents the edge between the faces  $a=(100)$  and  $b=(010)$ , and the arc  $bc$  represents the edge between the faces  $b=(010)$  and  $c=(001)$ , and as the axes have been chosen parallel to these edges, the angles between the edges will be equal to the axial angles. Therefore, the angle of intersection of the arcs  $ac$  (axis  $b$ ) and  $ab$  (axis  $c$ ) is the axial angle  $\alpha$ , that at the intersection of  $ab$  and  $bc$  (axis  $a$ ) is  $\beta$ , and that between  $bc$  and  $ac$  is  $\gamma$  (see Fig. 39). Hence, the three angles can at once be calculated when the three arcs  $ab$ ,  $bc$ , and  $ca$  are known, by the formulæ (a) of section (3), just given. The arcs in question will

<sup>1</sup> Fig. 54 is taken from the stereographic projection (already given in Fig. 48, on page 98) of methyl triphenylpyrrolone, a triclinic substance described by the author, *Journ. Chem. Soc.*, 1890, 57, 724.



generally be three of the five well-measured basal angles, but if any or all of them are not included in the basal angles, they can be calculated from any such five angles as are taken for the given data.

As regards the calculation of the **axial ratios**, the positions of at least two of the poles  $p = (110)$ ,  $m = (101)$ ,  $q = (011)$ , and  $o = (111)$  will probably have been included in the five basal angles, and those of the other two can be calculated with the aid of the formulæ of section (3), or, in cases where none are included in the given data, all can be so calculated. We shall then know the angular values of the whole of the arcs between the various poles shown in Fig. 54, and can, there-

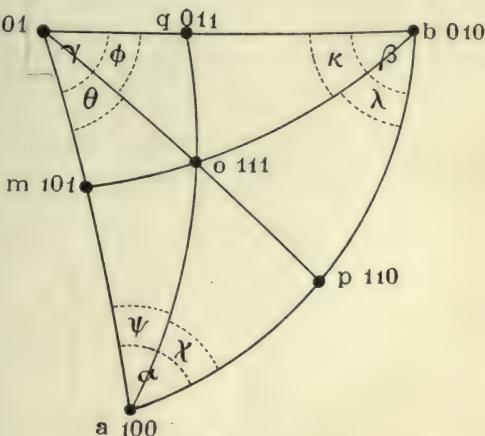


FIG. 54.

fore, calculate the angles  $\theta$  and  $\phi$ ,  $\chi$  and  $\psi$ ,  $\kappa$  and  $\lambda$ , shown on the figure, with the aid of the same formulæ, any five of the six angles  $ab$ ,  $bc$ ,  $ca$ ,  $oa$ ,  $ob$ ,  $oc$  being adequate for the purpose of such calculations. Then :

$$\frac{a}{b} = \frac{\sin \theta}{\sin \phi}; \quad \frac{c}{b} = \frac{\sin \psi}{\sin \chi}; \quad \frac{a}{c} = \frac{\sin \lambda}{\sin \kappa}.$$

The first two of these ratios suffice to give us the whole of the axial ratios  $a : b : c$ , for  $b$  is always taken as unity ; so that the quotient of the two sines, in the cases of the first two equations just given, expresses the required ratio of  $a$  or  $c$  to  $b$  directly. In the case of tetragonal crystals either the second equation for the ratio  $c : b$  or the third equation for  $a : c$  is alone sufficient, as in this system  $a = b$ .

That this simple calculation is correct can readily be shown. Fig. 40, which is reproduced in Fig. 55, represents the essential faces of a triclinic crystal, the three faces  $a$ ,  $b$ ,  $c$  being parallel to the axial planes and the fourth face  $o$  being the parametral plane ; while  $OX$ ,  $OY$ ,  $OZ$  are the axes. Further, the dotted triangle  $A$ ,  $B$ ,  $C$  represents a plane parallel to the parametral plane intercepting the axes  $a$ ,  $b$ ,  $c$  at  $A$ ,  $B$ ,  $C$ , and if a perpendicular to  $AB$  be dropped from  $O$ , namely,  $OD$ , then in the triangle  $OBA$  :

$$\frac{a}{b} = \frac{OA}{OB}; \quad \text{and} \quad \frac{\sin OBD}{\sin OAD} = \frac{\frac{OD}{OB}}{\frac{OD}{OA}} = \frac{OA}{OB} = \frac{a}{b}.$$

Now  $OBD$  is the angle between the edges  $ac$  (parallel to the axis  $b$ )

and  $co$ , which is the angle  $\theta$  in Fig. 54, and  $OAD$  is the angle between the edges  $bc$  (parallel to the axis  $a$ ) and  $co$ , which is the angle  $\phi$ , hence :

$$\frac{a}{b} = \frac{\sin \theta}{\sin \phi}.$$

In the same manner it can be readily be shown that :

$$\frac{c}{b} = \frac{\sin \psi}{\sin \chi} \text{ and } \frac{a}{c} = \frac{\sin \lambda}{\sin \kappa}.$$

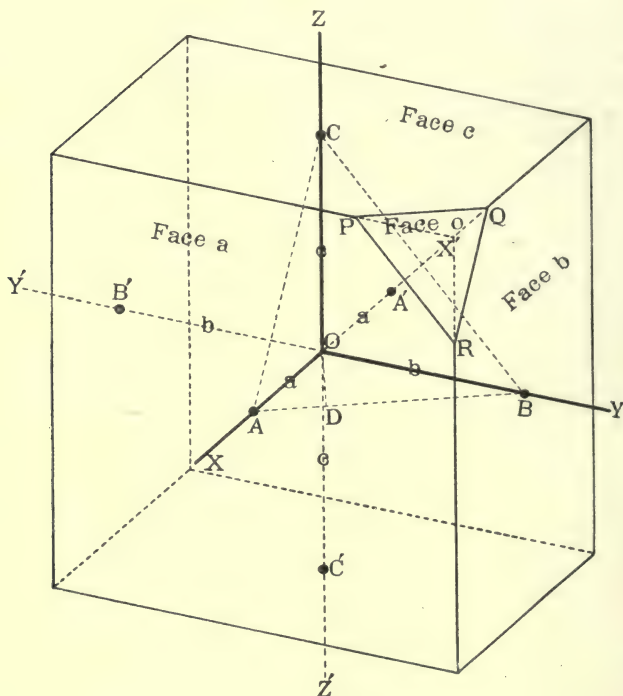


FIG. 55.

When any or all of the axial angles  $\alpha, \beta, \gamma$  are  $90^\circ$ , the calculation simplifies even further, to the simple tangent of an angle. Thus, when all three are  $90^\circ$ , as in the case of orthorhombic potassium sulphate :

$$\begin{aligned} \frac{a}{b} &= \frac{\sin \theta}{\sin \phi} = \frac{\sin ap}{\sin bp} = \frac{\sin ap}{\cos ap} = \tan ap. \\ \frac{c}{b} &= \frac{\sin \psi}{\sin \chi} = \frac{\sin cq}{\sin bq} = \frac{\sin cq}{\cos cq} = \tan cq. \end{aligned}$$

For the angle  $\theta$  is equal to  $ap = (100) : (110)$  when  $\gamma = 90^\circ$ , and  $\psi$  is similarly equal to the arc  $cq$  when  $\alpha = 90^\circ$ . Hence, the natural tangents

of the angles  $ap$  and  $cq$  at once give us the ratios of the axes  $a$  or  $c$  to unity (value of axis  $b$ ), which are the axial ratios required.

It will be obvious that in the case of a triclinic crystal the five most convenient angles to take for measured data are  $ab = (100) : (010)$ ,  $bc = (010) : (001)$ ,  $ca = (001) : (100)$ ,  $ap = (100) : (110)$ , and  $cq = (001) : (011)$ .

In the case of an orthorhombic crystal we really have the same five angles as basal data, for the first three are  $90^\circ$  by reason of the symmetry, and the fourth and fifth are the only possible variables, the measured values of which are taken as given basal data.

In the case of a monoclinic crystal, the ratio of two sines also simplifies to a simple tangent in the cases of  $\frac{a}{b}$  and  $\frac{c}{b}$ , which are the only two ratios we really require to calculate, for as  $b$  is taken as unity these two ratios give us  $a:b:c$  immediately. The sides of the primary triangle  $ab$  and  $bc$  are still  $90^\circ$  in a monoclinic crystal, the only side which is not  $90^\circ$  being  $ac$ . Hence the sum of  $\theta$  and  $\phi$  and also of  $\psi$  and  $\chi$  is  $90^\circ$ , and the sine of  $\phi$  and of  $\chi$  can be replaced by  $\cos \theta$  and  $\cos \psi$ , when  $\frac{a}{b} = \tan \theta$  and  $\frac{c}{b} = \tan \psi$ . The angles  $\theta$  and  $\psi$ , however, are not identical with the angular values of the arcs  $ap$  and  $cq$ , owing to the third axial angle not being  $90^\circ$ , and thus the calculation is not quite so simple as in the case of a rhombic crystal, where all three axial angles are  $90^\circ$ , for  $\theta$  and  $\psi$  have now to be calculated, by the use of Napier's rules, from the two right-angled triangles containing them. Three basal angles suffice for this purpose. An example will be fully worked out in Chapter XVII.

NOTE.—A chart for the rapid solution of spherical triangles when the three sides, or the two sides and the included angle, are known, was devised by Maurice d'Ocagne<sup>1</sup> in the year 1891; it has been reproduced in a size 15 inches square by G. W. Littlehales,<sup>2</sup> and may be obtained from Mr. Potter, Agent for Admiralty Charts, Minorities, London. It is graduated from  $5^\circ$  to  $175^\circ$  to single degrees, and over the greater part of the scale 6 minutes can be estimated, so that it serves admirably for the rapid checking of calculations. The particular cases of spherical triangle solutions with which it deals are just those which most frequently occur in crystallography.

<sup>1</sup> *Journal de l'École Polytechnique*, 1898, p. 224; *Traité de nomographie*, 1899, p. 328.

<sup>2</sup> *Vide* G. W. Littlehales in *Nature*, 1918, 102, 155; also A. Hutchinson, *loc. cit.*, 1919, 103, 25.



## CHAPTER VIII

### CALCULATION OF THE RESULTS OF THE GONIOMETRY OF THE TYPICAL CRYSTAL OF POTASSIUM SULPHATE

**A Complete Morphological Investigation of a Crystal** includes (1) the measurement of the angles between the faces along all the principal zones; (2) the calculation of the angles from the essential number—one, two, three, or five according to the system of symmetry on which the crystal is constituted—of well-measured angles, which are conveniently termed “basal angles,” and (3) the calculation of the axial angles and axial ratios, that is, of the elements of the crystal.

The general mode of carrying out (3) has just been described in the last section of Chapter VII. The calculation (2) is necessary because it is highly desirable to have this confirmation of the values of angles less frequently measured than the basal angles, or of angles between faces affording less perfect reflections. Also it often happens that certain faces may be missing altogether on a substance like potassium sulphate, but present on the crystals of other salts of the same isomorphous series, such as the sulphates of rubidium, cæsium, and ammonium, and the corresponding selenates; and it is highly desirable to compare the values of all these possible interfacial angles of all the salts of the series with one another. Moreover, besides the interfacial angles, the angles at the corners of the triangles are often needed for the calculation of the crystal elements, as has just been shown at the close of the last chapter.

With this preliminary explanation of the reason for the following calculations, and having in the first section of the last chapter set forth the chief formulæ required in their simplest guise, we may now pass directly to the calculations for the typical orthorhombic crystal of potassium sulphate, the practical goniometry of which was worked through in Chapter IV., and which forms an excellent and complete example of operation (1).

**Calculations of Interfacial Angles of Potassium Sulphate from two Basal Angles.**—The symmetry of the orthorhombic system, which will be described in Chapter XIV., and shown to consist, when fully developed, in the presence of three rectangular planes of symmetry, requires only two basal angles; given these, all the rest of the angles between actual

or possible faces of the crystal may be calculated, as well as the axial ratios. The three planes of symmetry being at right angles to each other, and their intersections being the axes, all three axial angles  $\alpha$ ,  $\beta$ ,  $\gamma$  are  $90^\circ$ , so that no calculation of axial angles is required for an orthorhombic crystal.

Besides the typical crystal of potassium sulphate the goniometry of which was thoroughly described in Chapter IV., ten others were measured by the author during the crystallographic investigation of that salt. In now proceeding to the calculations, the first thing is to choose which two of the angles measured shall be used as basal angles, and the two on which our choice will fall will be the two which proved uniformly most trustworthy, the faces yielding them having afforded in general the most excellent reflections of the Websky signal-slit, besides which these angles were among those of which the most numerous determinations, afforded by separate faces on all the eleven crystals, were made. The separate values for each angle should be set out in the note-book in a vertical column, the irreproachable "A" values being marked with their A; the arithmetical mean of the whole should then be taken, by adding up the column (if the degrees are the same only the minutes need be summed up) and dividing the result by the number of measurements, and the mean of the "A" values should also be separately found. If care has been taken to exclude altogether from consideration such values as were obtained from untrustworthy images of the signal, the two means should be, and in the case of potassium sulphate were, identical. This in itself is a proof of the careful selection of the crystals measured, and of the discrimination used in accepting the angular values included in the column of which the mean has been taken. Indeed some crystallographers would consider the whole of the accepted values as "A" values, but the author reserves this designation for values derived from truly splendid images, of the kind which would be yielded by optically worked truly plane glass surfaces.

With regard to this taking of means, however, it cannot be too strongly emphasised that this is only to be done *after* the question of the symmetry has been settled, and it is quite certain that the angles the mean of which is being taken are actually such as are intended, in conformity with the proved and accepted symmetry, to be identical in value. In the cases of certain zones on a rhombic crystal such as one of potassium sulphate it is possible for each angle to be repeated four times in the zone, afforded by quite different but symmetrically situated faces, and as the zones themselves may occur in duplicate, symmetrically arranged on each side of a plane of symmetry, each of the angles may thus occur eight times on the same crystal. When ten crystals are measured (eleven were measured in the case of potassium sulphate), the number of repetitions of the same angles may reach as many as eighty. When describing the measurement of the potassium sulphate crystal in Chapter IV., stress was laid on the important rule just referred to as regards the legitimacy of extraction of mean values, and the proper mode of considering the indications of the measurements as to the symmetry

of the crystal was fully discussed. This, however, being all satisfactorily settled, and the whole of the possible eighty values agreed to be of equal value as regards the symmetry, it is quite legitimate to extract their mean.

The two basal angles chosen in the case before us of potassium sulphate are  $ao$  and  $co$ . The mean values of these angles derived from the crystal measured in Chapter IV., were respectively  $43^\circ 52'$  and  $56^\circ 12'$ . Those derived from the whole eleven crystals were

respectively  $43^\circ 52'$  and  $56^\circ 11'$ , in the former case identical and in the latter only  $1'$  different. We shall, of course, employ the mean values derived from the whole eleven crystals as the basis of our calculations, which are to serve as a typical set. The angle  $ao$  had been measured sixty-eight times, and  $co$  no less than eighty times, in all instances from separate and independent faces.

As we shall require the stereographic projection before us continually during the process of making the calculations, as our guiding diagram, Fig. 38 is repeated in Fig. 56.

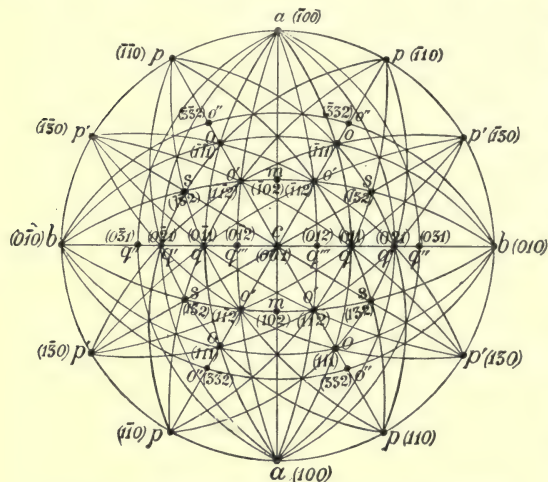


FIG. 56.—Stereographic Projection of Alkali Sulphates and Selenates.

continually during the process of making the calculations, as our guiding diagram, Fig. 38 is repeated in Fig. 56.

### Basal angles.

$$ao = (100) : (111) = 43^\circ 52',$$

$$co = (001) : (111) = 56^\circ 11'.$$

The knowledge of these angles at once implies that of two others, namely :

$$oq = (111) : (011) = 46^\circ 8',$$

$$op = (111) : (110) = 33^\circ 49'.$$

For  $ao$  and  $oq$  together make up  $90^\circ$ , as do also  $co$  and  $op$ .

To find the interfacial angle  $ap = (100) : (110)$ .

It will be convenient to commence with this angle, from our knowledge of three parts of the triangle  $aoc$ ; for in this triangle the side  $ac$  is a right angle, thus enabling us to use Napier's rules, and two other sides are the given basal angles  $ao$  and  $co$ . Moreover, the angle at  $c$  in this triangle is actually the angle  $ap$  itself. We first draw the usual Napierian diagram, as shown in Fig. 57. Then, by Napier's rules :



FIG. 57.



$$\cos 43^\circ 52' = \cos c \sin 56^\circ 11'$$

$$\text{or } \cos c = \frac{\cos 43^\circ 52'}{\sin 56^\circ 11'}$$

Working this out with the aid of a table of logarithms we have :

$$\text{Log. } \cos 43^\circ 52' \quad \bar{1} \cdot 85791$$

$$\text{Log. } \sin 56^\circ 11' \quad \bar{1} \cdot 91951$$

$$\text{Log. } \cos c \quad \bar{1} \cdot 93840$$

$$c = 29^\circ 48' = ap.$$

This value for  $ap$  is identical with the measured value, which was the mean of 29 measurements with different  $a$  and  $p$  faces. The mean of the four values derived from the typical crystal described in Chapter IV. was  $29^\circ 49'$ .

From our knowledge of  $ap$  we can at once get  $bp$ , for

$$bp = 90^\circ - 29^\circ 48' = 60^\circ 12'.$$

To find  $bp' = (010) : (130)$  and  $p'p = (130) : (110)$ .

In each quadrant  $ab$  of the primitive zone-circle there are four poles, namely,  $a$ ,  $p$ ,  $p'$ , and  $b$ , of which the positions of three are now known, namely  $a$ ,  $p$ , and  $b$ . Hence, we can immediately apply the theorem of the anharmonic ratio of four poles in a zone in order to find the fourth, and as one of the angles is  $90^\circ$  it will simplify to the product or quotient of two tangents. The conditions are shown diagrammatically in Fig. 58. Setting down the anharmonic ratio we have :

$$\frac{\sin ap}{\sin ap'} \cdot \frac{\sin bp'}{\sin bp} = \frac{110}{100} \cdot \frac{130}{010}$$

$$\text{or } \frac{\sin ap}{\cos bp'} \cdot \frac{\sin bp'}{\cos ap} = \frac{1}{3} \cdot \frac{1}{1}$$

$$\text{or } \tan ap \cdot \tan bp' = \frac{1}{3}, \text{ from which we get}$$

$$\tan bp' = \frac{1}{3} \cot ap = \frac{1}{3} \cot 29^\circ 48'.$$

Working this out by logarithms we have :

$$\text{Log. } \cot 29^\circ 48' \quad 0 \cdot 24207$$

$$\text{Log. } 3 \quad 0 \cdot 47712$$

$$\text{Log. } \tan bp' \quad \bar{1} \cdot 76495$$

$$bp' = 30^\circ 12'.$$

$$\text{Then } p'p = bp - bp' = 60^\circ 12' - 30^\circ 12' = 30^\circ 0'.$$

The mean of 32 independent measurements of  $bp'$  was  $30^\circ 11'$ , and of 30 separate measurements of  $p'p$   $30^\circ 0'$ , the agreement between the calculated and measured values being again eminently satisfactory. The mean of the four independent values of  $bp'$  yielded by the typical crystal was  $30^\circ 12'$ , and of the four of  $p'p$   $29^\circ 59'$ .

To find  $cq = (001) : (011)$ .

In the triangle  $cog$  we know the angle at  $c$ , for it is the same as  $bp$ , namely,  $60^\circ 12'$ , also the angles  $og = 46^\circ 8'$  and  $co = 56^\circ 11'$ . Moreover, the angle at  $q$  is a right angle, for it is at the intersection of two mutually rectangular zones  $[cqb]$  and  $[aoq]$ . Setting out, therefore,

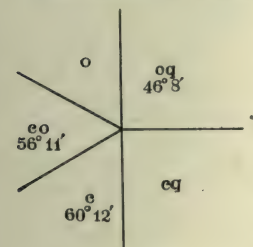


FIG. 59.

the Napierian diagram, Fig. 59, we find that the most convenient pair of known angles to employ will be  $og$  and  $c$ . Then, by Napier's rules we have :

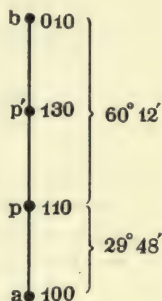


FIG. 58.

$$\sin cq = \tan 46^\circ 8' \cot 60^\circ 12'$$

$$\text{Log. } \tan 46^\circ 8' \quad 0.01719$$

$$\text{Log. } \cot 60^\circ 12' \quad \overline{1.75793}$$

$$\text{Log. } \sin cq \quad \overline{1.77512} \quad cq = 36^\circ 34'.$$

The mean of 16 measured angles  $cq$  was  $36^\circ 36'$ , and of the 4 values afforded by the typical crystal  $36^\circ 37'$ .

To find  $bq' = (010) : (021)$  and  $q'q = (021) : (011)$ .

We first find  $bq'$  from the anharmonic ratio of the four poles  $b$ ,  $q'$ ,  $q$ , and  $c$ , the whole angle  $bc$  being a right angle. With the aid of the diagram given in Fig. 60 we see that :

$$\begin{array}{c} b \bullet 010 \\ | \\ q' \bullet 021 \\ | \\ q \bullet 011 \\ | \\ c \bullet 001 \end{array} \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \begin{array}{l} 53^\circ 26' \\ \\ 36^\circ 34' \end{array}$$

$$\frac{\sin 36^\circ 34'}{\sin cq'} \cdot \frac{\sin bq'}{\sin bq} = \frac{011}{001} \cdot \frac{021}{010} = \frac{021}{011}$$

Now  $\sin cq' = \cos bq'$ , and  $\sin bq = \cos cq$ , hence :

$$\frac{\sin 36^\circ 34'}{\cos bq'} \cdot \frac{\sin bq'}{\cos 36^\circ 34'} = \frac{1}{2} \cdot \frac{1}{1},$$

$$\text{or } \tan 36^\circ 34' \tan bq' = \frac{1}{2},$$

$$\text{or } \tan bq' = \frac{1}{2} \cot 36^\circ 34'$$

$$\text{Log. } \cot 36^\circ 34' \quad 0.12973$$

$$\text{Log. } 2 \quad 0.30103$$

$$\text{Log. } \tan bq' \quad \overline{1.82870} \quad bq' = 33^\circ 59'.$$

This value is identical with the mean value of 30 independent measurements, and the mean of the four  $bq'$  angles on the typical crystal was  $33^\circ 58'$ , only  $1'$  removed.

Then  $q'q = bq - bq' = 53^\circ 26' - 33^\circ 59' = 19^\circ 27'$ .

The mean of 16 measured values was  $19^\circ 26'$ , and of the 4 values derived from the typical crystal  $19^\circ 25'$ .

To find  $bq'' = (010) : (031)$  and  $q''q' = (031) : (021)$ .

The pole  $q''$  is obviously of the same character as  $q'$  in the zone  $[bqc]$ , but  $q''$  has the position corresponding to the indices (031), whereas  $q'$  has that corresponding to (021). Hence we can find  $bq''$  by considering it as the second pole in the zone of four poles just dealt with, instead of  $q'$ , and we can use the same formula, only substituting  $\frac{1}{3}$  for  $\frac{1}{2}$  as the numerical value of the right-hand side obtained by cross-multiplication of the indices. The final formula then reduces to :

$$\tan bq'' = \frac{1}{3} \cot 36^\circ 34'.$$

$$\text{Log. } \cot 36^\circ 34' \quad 0.12973$$

$$\text{Log. } 3 \quad 0.47712$$

$$\text{Log. } \tan bq'' \quad \overline{1.65261} \quad bq'' = 24^\circ 12'.$$

Then  $q''q' = bq' - bq'' = 33^\circ 59' - 24^\circ 12' = 9^\circ 47'$ .

The above value of  $bq''$  is identical with that of the single measurement of this angle obtained with the typical crystal, and the mean value derived from 8 measurements was only  $1'$  removed, namely,  $24^\circ 13'$ .

The value of  $q''q'$  measured once on the typical crystal was  $9^\circ 44'$ , as was also the mean of 7 independent values derived from 7 different crystals, each of which exhibited only one face of this form.

It is useful and interesting to mention here that another face is found

developed in the zone  $[cqb]$  besides  $q'=(021)$  and  $q''=(031)$ , namely,  $q'''=(012)$ , between  $c$  and  $q$ , in the cases of certain other salts of the isomorphous series of alkali sulphates and selenates, to which potassium sulphate belongs, namely, on ammonium sulphate, rubidium sulphate, thallium sulphate, and cæsium selenate. It is shown on the stereographic projection in Fig. 56, which is the general figure for the series. It was not, however, observed on the eleven crystals of potassium sulphate investigated. Being a possible face, however, and occurring on certain members of the series, it was desirable to calculate the value of the angles  $cq'''$  and  $q'''q$  for all the salts of the series so that a comparison of these angles could, as in the cases of all the others, be instituted. This is an excellent and most pertinent example of the value of such calculations of crystal angles from basal angles.

We shall, therefore, include a calculation of the position of the pole  $q'''$ .

To find  $cq'''=(001):(012)$  and  $q'''q=(012):(011)$ .

The position of the rarer form  $q'''$  in the zone  $[cqb]$  is found by considering it as the fourth pole in that zone quadrant. The diagram is given in Fig. 61, and the corresponding anharmonic ratio is :

$$\frac{\sin 53^{\circ} 26'}{\sin bq'''} \cdot \frac{\sin cq'''}{\sin 36^{\circ} 34'} = \frac{010}{010} \cdot \frac{001}{001},$$
$$\frac{\sin 53^{\circ} 26'}{\cos cq'''} \cdot \frac{\sin cq'''}{\cos 53^{\circ} 26'} = \frac{1}{2} \cdot \frac{1}{1},$$
$$\tan 53^{\circ} 26' \tan cq''' = \frac{1}{2}$$
$$\tan cq''' = \frac{1}{2} \cot 53^{\circ} 26'.$$
$$\begin{array}{rcl} \text{Log. cot } 53^{\circ} 26' & \bar{1}.87027 \\ \text{Log. 2} & 0.30103 \\ \hline \text{Log. tan } cq''' & \bar{1}.56924 \end{array}$$

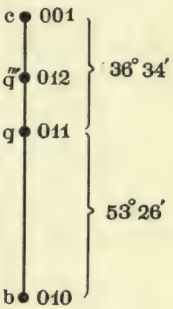


FIG. 61.

Then  $q'''q=cq-cq'''=36^{\circ} 34'-20^{\circ} 21'=16^{\circ} 13'$ .

To find  $co'=(001):(112)$  and  $o'o=(112):(111)$ .

We can here again use the anharmonic ratio of four poles in a zone, of which the extreme poles  $c$  and  $p$  are  $90^{\circ}$  apart, the diagram for which is given in Fig. 62.

From this, using  $\cos co'$  instead of  $\sin po'$ , and  $\cos 33^{\circ} 49'$  instead of  $\sin 56^{\circ} 11'$ , we at once get :

$$\frac{\sin 33^{\circ} 49'}{\cos co'} \cdot \frac{\sin co'}{\cos 33^{\circ} 49'} = \frac{111}{110} \cdot \frac{112}{001},$$
$$\tan 33^{\circ} 49' \tan co' = \frac{1}{2}$$
$$\tan co' = \frac{1}{2} \cot 33^{\circ} 49'.$$

$$\begin{array}{rcl} \text{Log. cot } 33^{\circ} 49' & 0.17401 \\ \text{Log. 2} & 0.30103 \\ \hline \text{Log. tan } co' & \bar{1}.87298 \end{array}$$

$co'=36^{\circ} 44'$ .

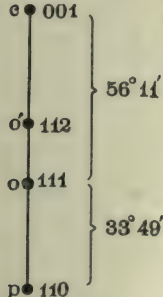


FIG. 62.

Then  $o'o=co-co'=56^{\circ} 11'-36^{\circ} 44'=19^{\circ} 27'$ .



The mean of the eight values of the latter angle measured on the typical crystal was identical with this value  $19^\circ 27'$ , and the mean of 37 measurements on the whole eleven crystals was only  $1'$  removed, namely,  $19^\circ 26'$ . The mean of 8 angles  $co'$  on the typical crystal, and also of 35 measurements of  $co'$  on the whole of the crystals, was  $36^\circ 45'$ , only  $1'$  removed again from the calculated value.

To find  $po' = (110) : (332)$  and  $o''o = (332) : (111)$ .

Using again the formula for four poles in a zone, and choosing as the three other than  $o''$  the poles  $c$  and  $p$ ,  $90^\circ$  apart, and  $o$ , as shown diagrammatically in Fig. 63, we have:

$$\frac{\sin po''}{\sin 33^\circ 49'} \cdot \frac{\sin 56^\circ 11'}{\sin co''} = \frac{110}{110} \cdot \frac{001}{001}$$

$$\frac{\sin po''}{\cos 56^\circ 11'} \cdot \frac{\sin 56^\circ 11'}{\cos po''} = \frac{2}{1} \cdot \frac{1}{3}$$

$$\tan po'' \tan 56^\circ 11' = \frac{2}{3}$$

$$\tan po'' = \frac{2}{3} \cot 56^\circ 11'$$

Log. 2	0.30103
Log. cot $56^\circ 11'$	$\bar{1}.82599$
	0.12702
Log. 3	0.47712
	Log. tan $po''$
	$\bar{1}.64990$

$$\frac{110}{110} \cdot \frac{001}{001} = \frac{332}{110} \cdot \frac{111}{332}$$

$$\frac{2}{1} \cdot \frac{1}{3}$$

$$po'' = 24^\circ 4'$$

FIG. 63.

Then  $o''o = po - po'' = 33^\circ 49' - 24^\circ 4' = 9^\circ 45'$ .

These values were only once measured, namely, on the typical crystal described in Chapter IV., the face  $o''$  being very rarely developed, and still more rarely with brilliantly reflecting surfaces. The measured values were  $24^\circ 0'$  and  $9^\circ 49'$ .

To find  $bo = (010) : (111)$ .

This angle is conveniently found from the right-angled triangle  $boc$ , in which the side  $bc$  is the right angle, and the side  $co$  and the angle at  $c$  (which is the same as the angle  $bp$  on the primitive circle) are known. From the Napierian diagram, Fig. 64, and Napier's rules we get:

$$\cos bo = \cos 60^\circ 12' \sin 56^\circ 11'$$

$$\text{Log. } \cos 60^\circ 12' \quad \bar{1}.69633$$

$$\text{Log. } \sin 56^\circ 11' \quad \bar{1}.91951$$

$$\text{Log. } \cos bo \quad \bar{1}.61584 \quad bo = 65^\circ 37'.$$

Then

$$oo = (111) : (\bar{1}\bar{1}1) = 2[90^\circ - (65^\circ 37')] = 2(24^\circ 23') = 48^\circ 46'.$$

The mean values of the measured angles were respectively  $65^\circ 36'$  and  $48^\circ 47'$ , which show very satisfactory concordance with the calculated values.

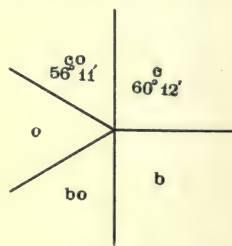


FIG. 64.

To find  $bo' = (010) : (112)$ .

This angle is similarly found from the triangle  $bo'c$ , which has likewise the same right angle for the side  $bc$  and the same angle at  $c$ , and  $co'$  is also known. The Napierian diagram is given in Fig. 65, and, applying Napier's rules, we obtain:

$$\begin{aligned}\cos bo' &= \cos 60^\circ 12' \sin 36^\circ 44' \\ \text{Log. } \cos 60^\circ 12' & \quad \bar{1} \cdot 69633 \\ \text{Log. } \sin 36^\circ 44' & \quad \bar{1} \cdot 77677 \\ \hline \text{Log. } \cos bo' & \quad \bar{1} \cdot 47310 \quad bo' = 72^\circ 42'.\end{aligned}$$

Then

$$o'o' = (112) : (1\bar{1}2) = 2[90^\circ - (72^\circ 42')] = 2(17^\circ 18') = 34^\circ 36'.$$

These values are identical with the mean of all the measured angles  $bo'$  and  $o'o'$ .

To find  $ao' = (100) : (112)$ .

This is achieved from the right-angled triangle  $ao'c$ , in which the side  $ac$  is the right angle, the side  $co'$  is known, and the angle at  $c$  is also known because it is the same as the angle  $ap$  on the primitive circle.

The diagram is given in Fig. 66, and by Napier's rules we obtain from it :

$$\begin{aligned}\cos ao' &= \cos 29^\circ 48' \sin 36^\circ 44' \\ \text{Log. } \cos 29^\circ 48' & \quad \bar{1} \cdot 93840 \\ \text{Log. } \sin 36^\circ 44' & \quad \bar{1} \cdot 77677 \\ \hline \text{Log. } \cos ao' & \quad \bar{1} \cdot 71517 \quad ao' = 58^\circ 44'.$$

Then

$$o'o' = (112) : (\bar{1}12) = 2[90^\circ - (58^\circ 44')] = 2(31^\circ 16') = 62^\circ 32'.$$

The first of these angles is identical with the mean measured  $ao'$ , and the mean value of the measurements of  $o'o'$  was  $62^\circ 34'$ .

We now come to the calculation of the angles in the subsidiary zones the zone circles of which pass through the poles of the prism faces  $p$  and  $p'$ .

To find  $po = (110) : (1\bar{1}1)$  and  $q'p = (0\bar{2}1) : (1\bar{1}0)$  in the zone  $[poq'p]$ .

The angle  $po$  can be found from the right-angled triangle  $p = (110)$ ,  $o = (1\bar{1}1)$ ,  $p = (1\bar{1}0)$ , the diagram being given in Fig. 67. By Napier's rules we have :

$$\begin{aligned}\cos po &= \cos 33^\circ 49' \cos 59^\circ 36' \\ \text{Log. } \cos 33^\circ 49' & \quad \bar{1} \cdot 91951 \\ \text{Log. } \cos 59^\circ 36' & \quad \bar{1} \cdot 70418 \\ \hline \text{Log. } \cos po & \quad \bar{1} \cdot 62369 \quad po = 65^\circ 8'.$$

The angle  $q'p$  can similarly be found from the right-angled triangle  $b = (010)$ ,  $q' = (021)$ ,  $p = (110)$ , the diagram being given in Fig. 68. From this we obtain :

$$\begin{aligned}\cos q'p &= \cos 60^\circ 12' \cos 33^\circ 59' \\ \text{Log. } \cos 60^\circ 12' & \quad \bar{1} \cdot 69633 \\ \text{Log. } \cos 33^\circ 59' & \quad \bar{1} \cdot 91866 \\ \hline \text{Log. } \cos q'p & \quad \bar{1} \cdot 61499 \quad q'p = 65^\circ 40'.$$

Then

$$oq' = [180 - (65^\circ 8' + 65^\circ 40')] = (180^\circ - 130^\circ 48') = 49^\circ 12'.$$

The mean values of the measured angles  $po$ ,  $oq'$ , and  $q'p$  were respectively  $65^\circ 9'$ ,  $49^\circ 11'$ , and  $65^\circ 40'$ , the concordance being eminently satisfactory.

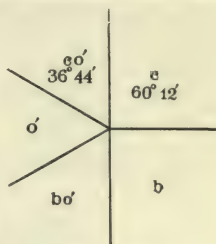


FIG. 65.

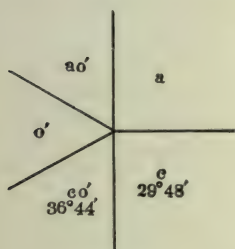


FIG. 66.

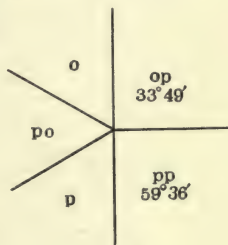


FIG. 67.

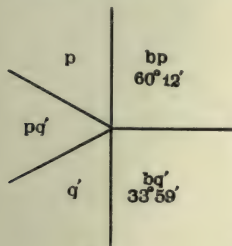


FIG. 68.

To find  $po' = (110) : (\bar{1}\bar{1}2)$  and  $qp = (0\bar{1}1) : (\bar{1}\bar{1}0)$  in the zone  $[po'qp]$ .

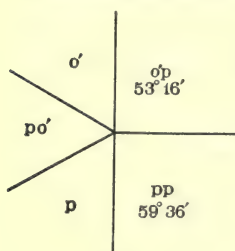


FIG. 69.

The angle  $po'$  is found from the triangle  $p=(110)$ ,  $o'=(\bar{1}\bar{1}2)$ ,  $p=(\bar{1}\bar{1}0)$ , in which the angle at  $p=(\bar{1}\bar{1}0)$  is a right angle, the side  $p=(\bar{1}\bar{1}0) : o'=(\bar{1}\bar{1}2)$  is known to be  $90^\circ - co' = 53^\circ 16'$ , and the side  $pp = 2ap = 59^\circ 36'$ .

The diagram is set out in Fig. 69, and by the rules we at once obtain :

$$\begin{aligned} \cos po' &= \cos 53^\circ 16' \cos 59^\circ 36' \\ \text{Log. } \cos 53^\circ 16' & \quad \bar{1}.77677 \\ \text{Log. } \cos 59^\circ 36' & \quad \bar{1}.70418 \\ \hline \text{Log. } \cos po' & \quad \bar{1}.48095 \quad po' = 72^\circ 23'. \end{aligned}$$

The angle  $pq$  is obtained from the triangle  $bqp$ , in which the angle at  $b$  is a right angle,  $bq$  is  $90^\circ - cq = 53^\circ 26'$  and  $bp$  is  $60^\circ 12'$ .

The diagram will be found in Fig. 70, and from the rules the equation required is :

$$\begin{aligned} \cos pq &= \cos 53^\circ 26' \cos 60^\circ 12' \\ \text{Log. } \cos 53^\circ 26' & \quad \bar{1}.77507 \\ \text{Log. } \cos 60^\circ 12' & \quad \bar{1}.69633 \\ \hline \text{Log. } \cos pq & \quad \bar{1}.47140 \quad pq = 72^\circ 47'. \end{aligned}$$

Then

$$o'q = [180^\circ - (72^\circ 23' + 72^\circ 47')] = (180^\circ - 145^\circ 10') = 34^\circ 50'.$$

The mean measured values of these three angles were respectively  $72^\circ 23'$ ,  $72^\circ 46'$ , and  $34^\circ 52'$ .

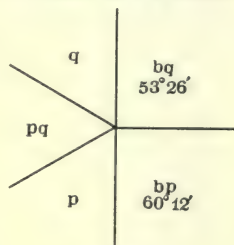


FIG. 70.

To find  $p'o = (130) : (111)$ ,  $oo' = (111) : (\bar{1}\bar{1}2)$ ,  $o'q' = (\bar{1}\bar{1}2) : (0\bar{2}1)$ , and  $q'p' = (0\bar{2}1) : (\bar{1}\bar{1}30)$  in the zone  $[p'oo'q'p']$ .

The angle  $p'o$  is found from the triangle  $p=(110)$ ,  $o=(111)$ ,  $p'=(130)$ , in which the angle at  $p$  is a right angle, and the sides  $op$  and  $pp'$  are respectively known to be  $33^\circ 49'$  and  $30^\circ 0'$ . The diagram is given in Fig. 71, and from Napier's rules we get :

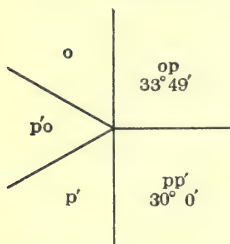


FIG. 71.

The angle  $p'q'$  may next be conveniently found from the triangle  $b=(010)$ ,  $q'=(021)$ ,  $p'=(130)$ , in which there is a right angle at  $b$ , and the sides  $bq'$  and  $bp'$  are known to be respectively  $33^\circ 59'$  and  $30^\circ 12'$ . The Napierian diagram is given in Fig. 72, and from the rules we obtain :

$$\begin{aligned} \cos p'q' &= \cos 33^\circ 59' \cos 30^\circ 12' \\ \text{Log. } \cos 33^\circ 59' & \quad \bar{1}.91866 \\ \text{Log. } \cos 30^\circ 12' & \quad \bar{1}.93665 \\ \hline \text{Log. } \cos p'q' & \quad \bar{1}.85531 \quad p'q' = 44^\circ 13'. \end{aligned}$$

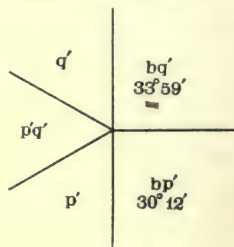


FIG. 72.

Thus far we have been able to calculate the whole of the angles with the aid only of the principle of four poles in a zone and Napier's rules for right-angled triangles. We now meet with a case, in the calculation of the angle



$q'o'$ , which requires the use of an oblique-angled triangle,  $c=(001)$ ,  $q'=(0\bar{2}1)$ ,  $o'=(1\bar{1}2)$ , in which we know the two sides  $cq'=56^\circ 1'$  and  $co'=36^\circ 44'$ , and the angle between them at  $c$  for this is the same as  $bp$  on the primitive circle,  $60^\circ 12'$ . The case is that of ( $b$ ) section (3) of the last chapter, and employing the formulæ there given we have:

$$\begin{aligned}\tan \theta &= \tan 36^\circ 44' \cos 60^\circ 12' \\ \cos q'o' &= \frac{\cos 36^\circ 44' \cos (56^\circ 1' - \theta)}{\cos \theta}\end{aligned}$$

Log. $\tan 36^\circ 44'$	1̄.87290	Log. $\cos 36^\circ 44'$	1̄.90386
Log. $\cos 60^\circ 12'$	1̄.69633	Log. $\cos 35^\circ 40'$	1̄.90978
Log. $\tan \theta$	1̄.56923		1̄.81364
$\theta = 20^\circ 21'$		Log. $\cos \theta$	1̄.97201
		Log. $\cos q'o'$	1̄.84163 $q'o' = 46^\circ 1'$

Then the remaining angle of the zone,  $oo'$ , is the difference of  $180^\circ$  and the sum of the three angles  $p'o$ ,  $p'q'$ , and  $q'o'$  just calculated, that is:

$$oo' = (111) : (1\bar{1}2) = 180^\circ - 134^\circ 13' = 45^\circ 47'.$$

These values for  $p'o$ ,  $p'q'$ , and  $oo'$  are identical with the mean measured angles, and the measured mean for  $q'o'$  was  $46^\circ 0'$ , only  $1'$  removed from the calculated value.

To find  $p'o' = (130) : (112)$ ,  $o'q = (112) : (0\bar{1}1)$ , and  $qp' = (0\bar{1}1) : (1\bar{3}0)$  in the final zone  $[p'o'qp']$ .

The value of  $p'o'$  can be readily found from the right-angled triangle  $p=(110)$ ,  $o'=(112)$ ,  $p'=(130)$ , in which the right angle is at  $p$ , and  $op$  and  $pp'$  are respectively known to be  $53^\circ 16'$  and  $30^\circ 0'$ .

The diagram is given in Fig. 73, and by the rules we get:

$$\begin{aligned}\cos p'o' &= \cos 53^\circ 16' \cos 30^\circ 0' \\ \text{Log. } \cos 53^\circ 16' & 1̄.77677 \\ \text{Log. } \cos 30^\circ 0' & 1̄.93753 \\ \hline \text{Log. } \cos p'o' & 1̄.71430 \quad p'o' = 58^\circ 48' .\end{aligned}$$

The angle  $p'q$  can also be readily obtained from the triangle  $b=(010)$ ,  $q=(011)$ ,  $p'=(130)$ , in which there is a right angle at  $b$ , and  $bq=53^\circ 26'$  and  $bp'=30^\circ 12'$ .

From the diagram in Fig. 74 and Napier's rules we have:

$$\begin{aligned}\cos p'q &= \cos 53^\circ 26' \cos 30^\circ 12' \\ \text{Log. } \cos 53^\circ 26' & 1̄.77507 \\ \text{Log. } \cos 30^\circ 12' & 1̄.93665 \\ \hline \text{Log. } \cos p'q & 1̄.71172 \quad p'q = 59^\circ 0' .\end{aligned}$$

Then, finally,

$$o'q = [180^\circ - (58^\circ 48' + 59^\circ 0')] = 180^\circ - 117^\circ 48' = 62^\circ 12'.$$

The value for  $p'o'$  is identical with the mean of all the measured values. The mean measured value of  $o'q$  was  $62^\circ 14'$ , and that of  $qp'$  was  $58^\circ 58'$ , in each case only  $2'$  removed from the calculated values.

The whole of the interfacial angles of all the zones shown on the stereographic projection, Fig. 56, page 116, have now been calculated from the two basal angles  $ao=(100) : (111) = 43^\circ 52'$ , and  $co=(001) : (111) = 56^\circ 11'$ , as given data. The calculation has been somewhat long, and

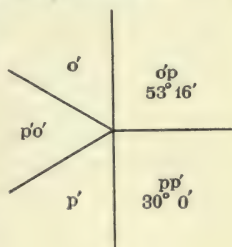


FIG. 73.

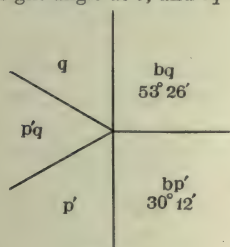


FIG. 74.

the logarithms have been actually quoted, as it was desired to work out a typical case completely from beginning to end with the minimum of trouble to the reader. It will have given a good idea how really simple such crystallographic calculations are, when the two principles of four poles in a zone and Napier's rules are grasped. Only in the case of one angle have these two principles proved inadequate, and required to be supplemented by the solution of an oblique-angled triangle. A very large proportion of crystals will prove to be similarly simple, and even in the cases of monoclinic crystals there will only be a very few angles for which oblique-angled triangles will have to be solved, and in every case they can be solved by the simple formulæ quoted in section (3) of the last chapter. A typical case of a monoclinic crystal will be worked through as an example in Chapter XVII. The cases of triclinic crystals will, of course, require the solution of numerous oblique-angled triangles, but it will be very rarely that the simple formulæ given in section (3) will require to be supplemented by others taken from a text-book of spherical trigonometry, and the principle of four poles in a zone will be of frequent application. A typically difficult triclinic crystal will also be calculated through in Chapter XIX. A crystal or a couple of crystals, in fact, will be worked out for each system of symmetry, in the chapter immediately following that describing the forms and classes of the system. In these subsequent cases, however, in order to save valuable space, the logarithms will not be quoted, but only the result of the working out of the equation given. The Napierian diagrams, and those for the anharmonic ratios, will also not need to be given in simple straightforward cases, but will be supposed to be drawn by the calculator personally, forming excellent exercises.

**Calculation of the Ratio of the Axes.**—In the case before us, of orthorhombic potassium sulphate, the ratios of the lengths of the axes  $a$  and

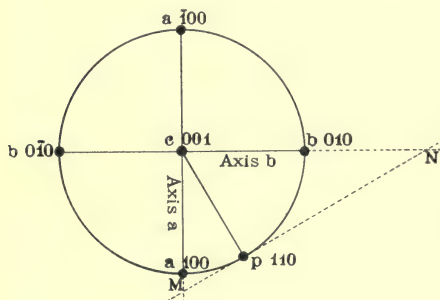


FIG. 75.

$c$  respectively to that of the axis  $b$  (considered as unity) are immediately given by the tangents of the angles of inclination of the two primary faces  $p = (110)$  and  $q = (011)$  to  $a$  and  $c$  respectively, as was shown near the close of the last chapter when considering the general mode of calculating axial ratios. Proceeding, however, from first principles, the conditions will be rendered clear by Fig. 75, which shows

the axes  $a$  and  $b$ , the poles of the  $a$  and  $b$  faces, and the pole of one of the faces of  $p = \{110\}$ . If the normal to the latter,  $cp$ , be drawn, and then a tangent to the circle at the point  $p$ , that is, a perpendicular to the normal, it will be obvious that the plane  $p = (110)$  is represented in plan by this tangent, and that it cuts the axes  $a$  and  $b$  prolonged at the points

M and N; the lengths  $cM$ ,  $cN$  will represent, therefore, the unit axial lengths, that is to say, the parameters, so  $\frac{cM}{cN}$  will be the ratio of the axes  $a : b$ . But this is the trigonometrical tangent of the angle  $cNM$ , and this angle is equal to the angle  $Mcp$ . Now this latter angle is the angle measured on the goniometer between the normals to  $a=(100)$  and  $p=(110)$ , in other words it is the angle  $ap=(100) : (110)$ .

Hence :

$$\frac{a}{b} = \tan ap = \tan 29^\circ 48' \\ = 0.5727.$$

Taking out the natural tangent of  $29^\circ 48'$  from a book of mathematical tables, we find it to be 0.5727. This, therefore, is the value of the ratio of the axes  $a$  and  $b$ . In a similar manner the ratio  $\frac{c}{b}$  is the tangent of the angle  $cq=(001) : (011)$ . That is :

$$\frac{c}{b} = \tan cq = \tan 36^\circ 34' = 0.7418.$$

The ratios of the three axes are thus :

$$a : b : c = 0.5727 : 1 : 0.7418.$$

**Tabular Presentation of Results.** — Having now completed our morphological investigation of the typical orthorhombic crystal of potassium sulphate, we should conclude by summarising the results in concise tabular form. In doing so, the results will be incorporated for the whole eleven crystals of this substance, which were employed in the author's complete investigation, and of which the crystal which has been worked through here as a typical one was the most perfect, in order that the table shall form an example of the manner in which such results for any substance crystallographically investigated should be presented for publication. The form of the table is that which has been agreed upon by the leaders of the subject in this country, and with the approval of Prof. von Groth, the distinguished founder and editor (until the year 1914) of the *Zeitschrift für Kristallographie*.

#### MORPHOLOGY OF CRYSTALS OF POTASSIUM SULPHATE, $K_2SO_4$ .

**Crystal-System :** Orthorhombic. **Crystal-Class** 8, rhombic holohedral.

**Habit :** Short prismatic parallel to the vertical axis  $c$ , or tabular parallel  $b=\{010\}$ , illustrated respectively by Figs. 1 and 2 (pages 3 and 6).

**Ratio of Axes :**  $a : b : c = 0.5727 : 1 : 0.7418$ .

**Forms observed :**  $a = \{100\}$ ,  $b = \{010\}$ ,  $c = \{001\}$ ,  $p = \{110\}$ ,  $p' = \{130\}$ ,  
 $q = \{011\}$ ,  $q' = \{021\}$ ,  $q'' = \{031\}$ ,  $o = \{111\}$ ,  $o' = \{112\}$ ,  
 $o'' = \{332\}$ .

**Table of Angles :** In the following table the basal angles are marked with an asterisk, and the angles in the same zone are recorded in their proper sequence and connected by an inclusive zonal bracket.



*Morphological Angles of Potassium Sulphate.*

Angle measured.	No. of Measurements.	Limits.	Mean observed.	Calculated.	Difference.
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (130) \\ p'b = (130) : (010) \end{array} \right.$	$\left\{ \begin{array}{l} 29 \\ 30 \\ 32 \end{array} \right.$	$\left\{ \begin{array}{l} 29 \ 45 - 29 \ 52 \\ 29 \ 55 - 30 \ 4 \\ 30 \ 8 - 30 \ 15 \end{array} \right.$	$\left\{ \begin{array}{l} 29 \ 48 \\ 30 \ 0 \\ 30 \ 11 \end{array} \right.$	$\left\{ \begin{array}{l} 29 \ 48 \\ 30 \ 0 \\ 30 \ 12 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 0 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} cq''' = (001) : (012) \\ q'''q = (012) : (011) \\ cq = (001) : (011) \\ qq' = (011) : (021) \\ cq' = (001) : (021) \\ q'q'' = (021) : (031) \\ q''b = (031) : (010) \\ q'b = (021) : (010) \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ \dots \\ 16 \\ 16 \\ 29 \\ 7 \\ 8 \\ 30 \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ \dots \\ 36 \ 31 - 36 \ 41 \\ 19 \ 20 - 19 \ 31 \\ 55 \ 55 - 56 \ 9 \\ 9 \ 40 - 9 \ 55 \\ 24 \ 7 - 24 \ 19 \\ 33 \ 52 - 34 \ 5 \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ \dots \\ 36 \ 36 \\ 19 \ 26 \\ 56 \ 2 \\ 9 \ 44 \\ 24 \ 13 \\ 35 \ 49 \end{array} \right.$	$\left\{ \begin{array}{l} 20 \ 21 \\ 16 \ 13 \\ 36 \ 34 \\ 19 \ 27 \\ 56 \ 1 \\ 9 \ 47 \\ 24 \ 12 \\ 33 \ 59 \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ \dots \\ 2 \\ 1 \\ 1 \\ 3 \\ 1 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \end{array} \right.$	$\left\{ \begin{array}{l} 68 \\ 58 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \ 45 - 44 \ 0 \\ 46 \ 4 - 46 \ 15 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \ 52 \\ 46 \ 8 \end{array} \right.$	$\left\{ \begin{array}{l} * \\ 46 \ 8 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} ao' = (100) : (112) \\ o'o' = (112) : (112) \end{array} \right.$	$\left\{ \begin{array}{l} 27 \\ 7 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \ 38 - 58 \ 47 \\ 62 \ 30 - 62 \ 38 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \ 44 \\ 62 \ 34 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \ 44 \\ 62 \ 32 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 2 \end{array} \right.$
$\left\{ \begin{array}{l} bo = (010) : (111) \\ oo = (111) : (111) \end{array} \right.$	$\left\{ \begin{array}{l} 73 \\ 33 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 32 - 65 \ 41 \\ 48 \ 40 - 48 \ 52 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 36 \\ 48 \ 47 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 37 \\ 48 \ 46 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} bo' = (010) : (112) \\ o'o' = (112) : (112) \end{array} \right.$	$\left\{ \begin{array}{l} 25 \\ 7 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 38 - 72 \ 48 \\ 34 \ 31 - 34 \ 41 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 42 \\ 34 \ 36 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 42 \\ 34 \ 36 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} co' = (001) : (112) \\ o'o = (112) : (111) \\ co = (001) : (111) \\ oo'' = (111) : (332) \\ o''p = (332) : (110) \\ op = (111) : (110) \end{array} \right.$	$\left\{ \begin{array}{l} 35 \\ 37 \\ 80 \\ 1 \\ 1 \\ 84 \end{array} \right.$	$\left\{ \begin{array}{l} 36 \ 38 - 36 \ 51 \\ 19 \ 16 - 19 \ 33 \\ 56 \ 6 - 56 \ 17 \\ - \\ - \\ 33 \ 42 - 33 \ 57 \end{array} \right.$	$\left\{ \begin{array}{l} 36 \ 45 \\ 19 \ 26 \\ 56 \ 11 \\ 9 \ 49 \\ 24 \ 0 \\ 33 \ 49 \end{array} \right.$	$\left\{ \begin{array}{l} 36 \ 44 \\ 19 \ 27 \\ * \\ 9 \ 45 \\ 24 \ 4 \\ 33 \ 49 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \\ - \\ 4 \\ 4 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} po = (110) : (111) \\ oq' = (111) : (021) \\ q'p = (021) : (110) \end{array} \right.$	$\left\{ \begin{array}{l} 55 \\ 45 \\ 49 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 2 - 65 \ 13 \\ 49 \ 6 - 49 \ 15 \\ 65 \ 32 - 65 \ 50 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 9 \\ 49 \ 11 \\ 65 \ 40 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \ 8 \\ 49 \ 12 \\ 65 \ 40 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} po' = (110) : (112) \\ o'q = (112) : (011) \\ qp = (011) : (110) \end{array} \right.$	$\left\{ \begin{array}{l} 21 \\ 15 \\ 23 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 19 - 72 \ 27 \\ 34 \ 49 - 34 \ 57 \\ 72 \ 43 - 72 \ 52 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 23 \\ 34 \ 52 \\ 72 \ 46 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 23 \\ 34 \ 50 \\ 72 \ 47 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 2 \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} p'o = (130) : (111) \\ oo' = (111) : (112) \\ o'q' = (112) : (021) \\ oq' = (111) : (021) \\ q'p' = (021) : (130) \end{array} \right.$	$\left\{ \begin{array}{l} 46 \\ 23 \\ 20 \\ 39 \\ 42 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \ 54 - 44 \ 6 \\ 45 \ 44 - 45 \ 52 \\ 45 \ 53 - 46 \ 7 \\ 91 \ 38 - 91 \ 55 \\ 44 \ 5 - 44 \ 23 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \ 59 \\ 45 \ 47 \\ 46 \ 0 \\ 91 \ 47 \\ 44 \ 13 \end{array} \right.$	$\left\{ \begin{array}{l} 43 \ 59 \\ 45 \ 47 \\ 46 \ 1 \\ 91 \ 48 \\ 44 \ 13 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 0 \\ 1 \\ 1 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} p'o' = (130) : (112) \\ o'q = (112) : (011) \\ qp' = (011) : (130) \end{array} \right.$	$\left\{ \begin{array}{l} 19 \\ 12 \\ 18 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \ 43 - 58 \ 53 \\ 62 \ 10 - 62 \ 18 \\ 58 \ 55 - 59 \ 1 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \ 48 \\ 62 \ 14 \\ 58 \ 58 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \ 48 \\ 62 \ 12 \\ 59 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 2 \\ 2 \end{array} \right.$
Total number of measurements	1160				

The excellent agreement between the calculated and observed values of the angles, as indicated by the fact that the greatest difference is only 4' and that only in the cases of three angles does it exceed 2', affords the best possible testimony to the accuracy of both the practical measurements and the calculations. It is of the character which may be expected when care has been taken that the crystals employed shall be of the highest attainable state of perfection.

## CHAPTER IX

### CRYSTAL SYMMETRY AND ITS 32 TYPES

It has been shown in Chapter V. that a crystal is characterised by the ratio  $a : b : c$  between the lengths of its axes  $a$ ,  $b$ ,  $c$ , and also by the angles  $\alpha$ ,  $\beta$ ,  $\gamma$  between those axes. It will be shown later, in Chapter XXX., that these axes may be regarded not only as the edges of intersection of the three primary facial planes, but also as those of the elementary parallelepipedon of the Bravais space-lattice, according to which the crystal structure is built up, in the cases of all but three of the fourteen space-lattices. It is, however, also characterised by its degree of symmetry, and certain of the above elements are fixed by that symmetry. The remainder have to be determined by goniometrical measurement, as described in Chapter IV., followed by calculation after the manner shown in Chapter VIII. It is necessary, therefore, that we should next study the types of crystal symmetry, which we shall find to be 32 in number, known as **Crystal Classes**. These 32 classes we shall further find may be grouped into 7 **Crystal Systems**, each group or system having a common arrangement of crystal axes.

One of the most important practical consequences of the satisfactory establishment of the geometrical theory of crystal structure, which will be dealt with in detail in Chapter XXX., was the abandonment of the previous mode of description of the crystal classes as holohedral (possessing the full symmetry of the system), hemihedral (in which half the full number of faces were supposed to be suppressed), and tetartohedral (in which one-fourth only of the holohedral faces were supposed to persist). It had been the custom to regard those classes of the 32 which did not exhibit the complete symmetry of one of the seven systems as derived by the suppression or latency of some of the faces, and the mode in which the suppression occurred, for it could generally happen in more than one way, determined the particular class. Even before the advent of the epoch-making work of Sohncke (described in Chapter XXX.), Victor von Lang had, in 1866, published his celebrated treatise (*Lehrbuch der Krystallographie*) in which the real elements of symmetry were indicated. In subsequent editions his work was strengthened and completed, embodying certain supplementary details arrived at by the mathematical genius

of Gadolin. Yet still, until even so late as the publication of the second edition of the *Physikalische Krystallographie* of P. Groth, Leipzig, 1885, the classification into holohedral, hemihedral, and tetartohedral classes still persisted. But after another decade, the year 1895, succeeding the completion of the work of Sohncke, Fedorov, Schönflies, and Barlow, saw the publication both of the third edition of Groth's book, and of another most valuable treatise, the *Morphology of Crystals*, by N. Story-Maskelyne, in both of which the 32 classes were treated as representing distinct types of symmetry, and not merely as fully or partially developed forms. Owing to the fact that the greater portion of the latter book had been a very long time in course of preparation, the transformation was but partial, for while insisting that axes and planes of symmetry are the true elements of symmetry, and clearly defining their real meaning, the terms holohedral, hemihedral, and tetartohedral were still employed. But in the third edition of Groth's book the 32 varieties were classified in their seven systems entirely by the method of and with reference to their development of planes and axes of symmetry, including the combination of the axis and plane as a plane of alternating symmetry as defined by Curie. Moreover, in a memoir in the *Neues Jahrbuch* for 1896, p. 495, a further strengthening was given to the new mode of description by Viola, who derived the elements of symmetry of the 32 classes of crystals by use of an entirely new method, that of quaternions. Thus supported in several ways from both the geometrical and the purely mathematical sides, the new mode of description, based upon the recognition of axes and planes of symmetry as the true elements of crystal symmetry, is now regarded as the only logical one, and the only one in full conformity with the completed geometrical theory of the homogeneous partitioning of space in a crystalline medium. Each of the 32 classes is now, therefore, described as definitely endowed with and characterised by its own specific planes and axes of symmetry, or by the absence of such; and the crystals conforming to subsidiary classes of any system, exhibiting less than the maximum symmetry and full number of faces possible to that system and formerly termed hemihedral or tetartohedral, are regarded as just as fully perfect individuals as those conforming to the class of maximum symmetry, and as exhibiting the complete symmetry which distinguishes their particular class, any idea of suppression of faces being altogether eliminated.

Thus the mode of description of the exterior symmetry of crystals, as well as the theory of their internal structure, which will be dealt with in Chapter XXX., are now both established on a logical and scientific basis. In proceeding to describe the 32 classes of crystals it will therefore, first of all, be advisable to define the elements of symmetry.

**Elements of Symmetry.**—The true elements of symmetry are “planes of symmetry” and “axes of symmetry.” The so-called “centre of symmetry” is not a true element of symmetry, although it is frequently convenient to use the term in connection with those holohedral triclinic crystals the faces of which are always duplicated in parallel pairs. Centrosymmetry, however, is merely the effect of rotation for  $180^\circ$  or for  $60^\circ$



about an axis of <sup>crystal</sup> symmetry followed by reflection across a plane of symmetry.

**Planes of Symmetry.**—If we imagine an ideal crystal with all the faces of each form equally developed, a “plane of symmetry” is such a plane as, passing through the centre of the crystal, would bisect it into equal halves. To every point on the crystal there corresponds a precisely analogous point at the same distance on the other side of the plane of symmetry. Also, when the one half is placed with the section plane against a plane mirror, the other half is apparently reproduced by reflection, so that either half may be considered as the mirror-image repetition of the other. A monoclinic crystal has only one such plane of symmetry, but a cubic crystal has no less than nine planes of symmetry, and between these limiting types there are several intermediate ones, which will presently be discussed.

Planes of symmetry are best recognised on the stereographic projection, for we have there the geometrical plan of the angular arrangement of the faces, uncomplicated by the usually promiscuously unequal development of the separate faces of the same form, which prevents the attainment, except by a very rarely, if ever, occurring chance, of the ideal equality of faces.

Every symmetry plane of a crystal is a possible face of the crystal, and the normal to a plane of symmetry is always a possible interfacial edge on the crystal.

**Axes of Symmetry.**—Besides reflection-repetition over a plane of symmetry, repetition of parts may occur by rotation about an axis.

An axis of symmetry is perpendicular to a possible face of the crystal, and is always a possible interfacial edge on the crystal.

There are four kinds of axes of symmetry, and only four, namely, digonal or binary, trigonal or ternary, tetragonal or quaternary, and hexagonal or senary; and they are such that rotation of the crystal about them for respectively  $180^\circ$ ,  $120^\circ$ ,  $90^\circ$ , and  $60^\circ$  brings the crystal again into a position of like aspect to that which it presented when in its original position.

Thus, when an octahedron is rotated for  $90^\circ$  about any one of the three diagonals, each face is brought into the position previously occupied by the adjoining one, and this will happen four times, at each interval of  $90^\circ$ , in a complete revolution of  $360^\circ$ . Such an axis of symmetry is a **tetragonal axis** or **axis of fourfold symmetry**.

These tetragonal axes of the octahedron are identical with the three rectangular axes of the cube and of the cubic system, and each of them is an axis in which four planes of symmetry intersect, namely, two of the three axial planes of symmetry and two of the six diagonal planes of symmetry bisecting the angles between the axial planes; such an axis of symmetry is therefore a tetragonal axis in two senses, and is called a **ditetragonal axis**.

Each of the four diagonals of the cube is similarly a **trigonal axis**, or **axis of threefold symmetry**, because during a complete rotation of  $360^\circ$  of the cube about any one of these diagonals it is brought three

times into a position which is indistinguishable from its original one. Moreover, as each of these four diagonals forms the line of intersection of the three planes of diagonal symmetry which pass through the same two corners as the diagonal in question, these trigonal axes of the cube are also so in two senses, and are therefore termed **ditrigonal axes**.

Similarly a **hexagonal axis** or **axis of sixfold symmetry** is such that a sixth of a complete revolution about it brings the crystal to exhibit again the same aspect, and it is termed a **dihexagonal axis** when it is also the intersection of the six planes of symmetry of a hexagonal crystal.

Lastly, a **digonal axis** or **axis of twofold symmetry** is such that half a complete revolution about it restores the original appearance of the crystal, and it is a **didigonal axis** when it also forms the line of intersection of two symmetry planes.

Indeed we may now define in general terms *di- $n$ -gonal symmetry*, by stating that an *n*-gonal axis which is the line of intersection of *n* planes of symmetry is termed a *di- $n$ -gonal axis of symmetry*.

In a similarly general manner we may also define four other terms currently employed concerning elements of symmetry, namely, *holoaxial*, *equatorial*, *alternating*, and *polar symmetry*, and which will also indicate four rules governing combinations of the elements of symmetry.

**Holoaxial symmetry** is present when an *n*-gonal axis is only accompanied by axes of digonal symmetry perpendicular to it, planes of symmetry being absent.

**Equatorial symmetry** is produced when an *n*-gonal axis is perpendicular to a plane of symmetry.

**Alternating symmetry** is arrived at by simultaneous rotation about an *n*-gonal axis and reflection across an equatorial plane. The equatorial plane in such a case is called a **plane of compound symmetry**.

**Polar symmetry** is that caused by the presence of an *n*-gonal axis which is perpendicular neither to a plane of symmetry nor to an axis of even symmetry. The two polar ends of a crystal endowed with only polar symmetry may be quite different from each other.

**Tesseral symmetry** is a term sometimes applied to the highest type of all possible crystal symmetry, that of the cubic system. It is specifically characterised by the four ditrigonal axes of symmetry.

Having now explained the terms currently used for the designation of the various elements of symmetry and their modes of combination, we can logically proceed to the classification of crystals according to their symmetry. It will be most instructive to show first of all how the other 31 classes of crystals are gradually evolved from the asymmetric class exhibiting absolutely no symmetry, by the introduction first of axes of symmetry alone, and then by the addition of planes of symmetry, until we eventually arrive at the perfect symmetry of the cubic system, in which we have the fullest possible combination of both elements of symmetry.

## THE 32 CLASSES OF CRYSTALS.

*Evolution of the other 31 Symmetric Classes from an Asymmetric Crystal (Class 1).*

The crystals of class 1, known as asymmetric, possess neither axes nor planes of symmetry, nor even exhibit the phenomenon of centrosymmetry due to the successive operation of both. Crystals of this class only satisfy the one condition of following the law of rational indices and the rules relating to zones.

The crystals of the whole of the other 31 classes possess symmetry, the degree of which continually ascends until we reach a holohedral crystal of the cubic system. Symmetry is unaltered by change of temperature, so that it is quite independent of the latter; for equal deformations are suffered in the symmetrical parts when the temperature alters. The crystals possessing symmetry may be first arranged in the following three groups:

- (1) Those the symmetry of which is brought about by rotation round an axis or axes of symmetry, but which possess no planes of symmetry.
- (2) Those possessing a plane or planes of symmetry.
- (3) Those the symmetry of which is derived by rotation about an axis of symmetry followed by mirror-image reflection from the plane perpendicular to the axis. This kind of symmetry plane is called a plane of compound symmetry, to distinguish it from an ordinary symmetry plane or plane of simple symmetry. It should be clearly understood that both operations occur in their entirety before reaching the second face. As in two of the three classes involved it results in centro-symmetry, crystals of this kind are sometimes said to possess a centre of symmetry. Centro-symmetrical crystals are, however, only special cases of the general principle underlying the symmetry of group (3).

There are 10 classes of group (1), and together with the asymmetric class 1 (making altogether 11 classes) they are distinguished by the property of **enantiomorphism**, which is brought about in all 11 classes by the absence of any plane of symmetry. An enantiomorphous crystal is one which by reflection in a plane mirror yields the image of a crystal similarly symmetrical and having equal angles, but laterally inverted; this second crystal cannot be got by rotation to resemble the first precisely, but behaves as a left hand does to a right one. The actual complementary crystal corresponding to this image would, analogously, furnish by reflection an image resembling the first variety. Both varieties of the crystals of one and the same chemical compound are known in the cases of many real substances.



The class number given for each class in the now following list refers to its order in the next list to be given, that in which the classes are arranged in their proper order in the seven crystal systems, and these class numbers are those which will be adhered to throughout this book. The order in which the classes are set out in this present list is merely one designed to render clear their evolution.

### GROUP 1.

#### *10 Enantiomorphous Classes without Planes of Symmetry but with one or more Axes of Symmetry.*

First come 4 classes with only one axis of symmetry, namely :

Crystals with 1 digonal	axis of symmetry	.	.	Class 4
„ „ 1 trigonal	„ „	.	.	„ 16
„ „ 1 tetragonal	„ „	.	.	„ 9
„ „ 1 hexagonal	„ „	.	.	„ 23

Next we have 6 classes with more than 1 axis of symmetry, namely :

Crystals with 1 digonal axis and 2 other digonal axes intersecting at 90° in the perpendicular plane.	Class 6.
„ „ 1 trigonal axis and 3 other digonal axes inclined at 60° in the perpendicular plane.	Class 18.
„ „ 1 tetragonal axis and 4 other digonal axes inclined at 45° in the perpendicular plane.	Class 11.
„ „ 1 hexagonal axis and 6 other digonal axes inclined at 30° in the perpendicular plane.	Class 24.
„ „ 3 perpendicular digonal axes and 4 trigonal axes meeting each other at equal angles.	Class 28.
„ „ 3 perpendicular tetragonal axes and 4 trigonal axes meeting each other at equal angles and also 6 digonal axes.	Class 29.

It may be stated in general terms that: If there be another axis of symmetry inclined to an  $n$ -gonal axis, there must be  $n$  such axes.

Enantiomorphism is always exhibited by substances which are capable of rotating the plane of polarised light, such as the two optically active (right- and left-handed) varieties of quartz and of tartaric acid, the right-handed and the left-handed varieties always corresponding to oppositely enantiomorphous crystals, which are the mirror-images of each other. When the optical activity is exhibited both by the crystals and by their solutions in solvents it is probably due to enantiomorphism both of the chemical molecules themselves and of the point-system governing the structure of the crystals.

The theory of point-systems reviewed in Chapter XXX. provides

completely for such cases, the arrangement of the points being screw-spiral-wise, either right or left. Such a structure can originate by the aggregation of molecules which are themselves enantiomorphous, in which case both the crystals and their solutions are optically active, as in the example, tartaric acid, just quoted, and as in the case of strychnine sulphate. But it may also happen that the enantiomorphism only applies to the point-system, and not to the chemical molecules, in which case the solution is inactive and the crystals alone rotate the plane of polarisation to the right or left, as in the case of sodium chlorate. There are also regular point-systems which exhibit the symmetry of one of the above 11 enantiomorphous classes, yet do not possess such screw axes, and are consequently optically inactive, both as regards the crystals and their solutions, as in the case of barium nitrate.

Hence, although all optically active substances afford enantiomorphous crystals, the inverse of the rule is not true, for enantiomorphous crystals are not always optically active. Some specific examples will be described and illustrated in later chapters, and the whole of Chapter L. will be devoted to the phenomenon of rotation of the plane of polarisation and the mode of measuring it.

## GROUP 2.

### *18 Classes of Crystals with a Plane or Planes of Symmetry, 17 of which have also an Axis or Axes of Symmetry.*

First come 4 classes of equatorial symmetry, that is, in which an  $n$ -gonal axis is perpendicular to a plane of symmetry.

- Crystals with a digonal axis and a symmetry plane perpendicular to it. Class 5.
- „ „ trigonal axis and a symmetry plane perpendicular to it. Class 19.
- „ „ tetragonal axis and a symmetry plane perpendicular to it. Class 12.
- „ „ hexagonal axis and a symmetry plane perpendicular to it. Class 25.

Next come 4 other classes having an  $n$ -gonal symmetry axis combined with as many symmetry planes as the  $n$  indicates.

- Crystals with a digonal axis and 2 symmetry planes intersecting in it at  $90^\circ$ . Class 7.
- „ „ trigonal axis and 3 symmetry planes intersecting in it at  $60^\circ$ . Class 20.
- „ „ tetragonal axis and 4 symmetry planes intersecting in it at  $45^\circ$ . Class 13.
- „ „ hexagonal axis and 6 symmetry planes intersecting in it at  $30^\circ$ . Class 26.

2 other classes are formed by adding to the two first of these four :

2 digonal axes perpendicular to the first and bisecting the angles of the 2 symmetry planes. Class 14.

3 digonal axes perpendicular to the trigonal axis and bisecting the angles of the 3 symmetry planes. Class 21.

We have next 4 further classes by combination of the first four classes of this group with the next four ; that is, in which in addition to the presence of an  $n$ -gonal axis and  $n$  symmetry planes intersecting in it, the plane perpendicular to the  $n$ -gonal axis is also a plane of symmetry. The four classes are respectively numbers 8, 22, 15, and 27.

Two further classes, numbers 30 and 31, are afforded in the special cases of the 3 perpendicular digonal axes of the ninth class of this group (class 14) being of equal length ; they are then the cube normals, and combinations of these axes with planes of symmetry are possible in two ways, according to one of which (class 30) the three cube faces are planes of symmetry, and according to the other of which (class 31) the 6 dodecahedron faces are the symmetry planes. In both cases the normals to the octahedron faces are trigonal symmetry axes.

Finally we have one class of the highest possible crystal symmetry, in which both kinds of planes, parallel to the 3 cube faces and to the 6 dodecahedron faces respectively, are symmetry planes. In this case the 3 cube normals are tetragonal axes of symmetry, the 4 octahedron normals are trigonal axes, and the 6 dodecahedron normals are digonal symmetry axes. This class is number 32.

The above are the 17 possible classes possessing both axes and planes of symmetry. To make up the 18 classes containing symmetry planes we have also 1 class of crystals characterised by the presence of 1 symmetry plane, without any symmetry axis. This is class 3.

We have now, in a manner which it is hoped has made clear the mode of evolution, dealt with 1 asymmetric class (class 1), 10 classes of group 1, and 18 classes of group 2, making altogether 29 classes.

The remaining 3 classes, forming group 3, of the whole 32 possible classes of crystals are those characterised by a plane of compound symmetry, or in other words, those formed by rotation about an axis followed immediately by reflection across a plane (a plane of compound symmetry). The axis must be one of even gonality, that is, di-, tetra-, or hexagonal, a trigonal axis being impossible under such circumstances.

### GROUP 3.

The first case, that of class 2, is formed by rotation about a digonal axis, which may be the normal of any face on the crystal, the plane of compound symmetry being parallel to the face. It is illustrated



in Fig. 76, in stereographic projection, the plane of the primitive circle being parallel to the face in question. The centre is then the projection of the pole of the digonal axis of symmetry. If any other face ( $hkl$ ) on the upper hemisphere of the crystal be represented by the dot, its equivalent face in the lower hemisphere, represented by the small ring, is arrived at by rotation of the dot-pole round the centre for  $180^\circ$  and then reflection at the plane of compound symmetry, the plane of the paper. The two faces are parallel and opposite, and may be said to be centro-symmetrical, but such a centre of symmetry is not essential to the presence of a plane of compound symmetry, as will appear when the next class is discussed. Fedorov has shown that the "centre of symmetry" is not a true element of symmetry, but merely the accompaniment of the operation of the general principle of reflection at a plane of compound symmetry in this special case of class 2 and a further one, class 17, the last of the three of this group.



FIG. 76.

The second case of this group, class 10, illustrated in Fig. 77, occurs when the axis of symmetry is a tetragonal one combined with a plane

of compound symmetry. Its pole is at the centre, and the plane of compound symmetry is again the plane of the primitive circle. If the dot in the right-front quadrant of the projection be the pole of a face ( $hkl$ ) in the upper hemisphere, rotation for  $90^\circ$  followed by reflection at the plane of compound symmetry brings us to the second face in the lower hemisphere, represented by a ring in the left-front quadrant; repetition of the process brings us to a face in the upper hemisphere again, represented by the dot-pole in the back-left quadrant, the opposite quadrant



FIG. 77.

to that started with, and two further repetitions bring us successively to a ring-pole-face in the lower hemisphere and to the original dot-pole-face in the upper hemisphere once more. The tetragonal axis of compound symmetry is thus also a digonal axis of ordinary symmetry. There are here no parallel faces, and there is, therefore, no centre of symmetry.

The third and last class of this group, class 17, involves the presence of a hexagonal axis and plane of compound symmetry, by the operation of which repetition occurs at every  $60^\circ$  with a change of hemisphere each time, the sixth repetition recovering the original position. Fig. 78 will render the case clear, the centre being the pole of the axis, and the three

dots and three rings alternately arranged being the poles of six faces in the successive sextants, situated alternately in the upper and lower hemispheres. The phenomenon of centrosymmetry happens here to be for the second time an accompaniment of the simultaneous operation of an axis of symmetry and a plane of compound symmetry. The hexagonal axis of compound symmetry is obviously also a trigonal axis of ordinary symmetry.

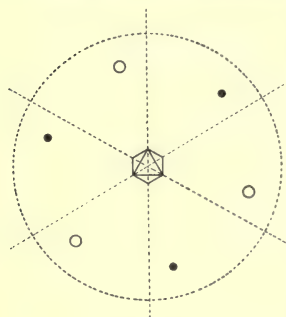


FIG. 78.

The 32 classes of crystal symmetry the evolution of which has now been followed are the only ones possible, if, as we must, we accept the law of rational indices as an experimental fact, irrespective of any theory of crystal structure. In practice, no crystal has ever yet been discovered which could

not be referred to one or other of these 32 classes. Examples of all the 32 classes are known, except class 19, the trigonal bipyramidal or trigonal equatorial class, of which no specimen has yet been found.

### *Division of the 32 Classes into*

#### 7 CRYSTAL SYSTEMS.

We have already seen that a *form* consists of all the faces of equal value with respect to the symmetry exhibited by the crystal, and it will now be apparent that the number of such faces belonging to one and the same form will be the greater the higher the degree of symmetry. The axes are usually so chosen that all the faces of a form will have the same numbers to represent their indices, only the signs being different for the faces in the different octants, and the order of the numbers when more than one face of the form occurs in the same octant. In the classes of higher symmetry all the faces having similar index numbers will belong to the same form, but not so in those of lower symmetry, in which cases only half, a quarter, or an eighth of such faces will belong to the same form, and in the asymmetric class only a single face belongs to a form. When the choice of axes is thus made, so that all the faces of equal value as regards the symmetry have equal index numbers, it is found that this choice happens in a similar way in the cases of several of the 32 classes, and that there are seven such ways. In other words, we find that the 32 classes fall into seven groups or "**systems**," the characteristic of each of which is a similar arrangement of crystal axes. It should be clear that the term axes in this paragraph refers to the fundamental crystallographic axes, parallel to 3 chosen interfacial edges, and the unit lengths of which are determined by the intercepts cut off along them by a parametral plane parallel to a fourth face inclined to all three axes. They may or may not be axes of symmetry. These seven systems are the triclinic, monoclinic, rhombic, trigonal,

tetragonal, hexagonal, and cubic systems. In the following scheme these seven systems are each separately analysed, their characteristics are indicated, the number of classes which each includes is specified, the actual class numbers (which in this list occur in their proper sequence) are given, and the symmetry elements of each of the 32 classes are recorded, together with the type of their symmetry. An example of each class is also quoted, except for class 19, the class not yet found developed.

### I. The Triclinic or Anorthic System.

Characterised by 3 inclined (otherwise than at  $90^\circ$ ,  $60^\circ$ ,  $45^\circ$ , or  $30^\circ$ ) unequal axes,  $a$ ,  $b$ ,  $c$ .

$$a : b : c = ? : 1 : ? \quad \alpha = ? \quad \beta = ? \quad \gamma = ?$$

Includes 2 classes.

Class 1. Asymmetric class. No symmetry.

*Example*—Calcium thiosulphate,  $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ .

Class 2. Pinakoidal or holohedral class. A digonal axis and a plane of compound symmetry perpendicular to it, which are equivalent to a centre of symmetry.

*Example*—Copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

### II. The Monoclinic or Monosymmetric System.

Characterised by 3 unequal axes, two of which,  $a$  and  $c$ , are inclined, but the third  $b$  is perpendicular to those two.

$$a : b : c = ? : 1 : ? \quad \alpha = \gamma = 90^\circ, \beta = ?$$

Includes 3 classes.

Class 3. Domal class. A plane of symmetry.

*Example*—Potassium tetrathionate,  $\text{K}_2\text{S}_4\text{O}_6$ .

Class 4. Sphenoidal Class. Type, digonal polar. A digonal axis.

*Example*—Tartaric acid,  $\text{C}_4\text{H}_6\text{O}_6$ , two oppositely enantiomorphous forms, dextro and lævo.

Class 5. Prismatic or holohedral class. Type, digonal equatorial. A symmetry plane and a digonal axis perpendicular to it.

*Example*—Potassium magnesium sulphate,  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

### III. The Rhombic or Orthorhombic System.

Characterised by 3 unequal but rectangular axes,  $a$ ,  $b$ ,  $c$ .

$$a : b : c = ? : 1 : ? \quad \alpha = \beta = \gamma = 90^\circ.$$

Includes 3 classes.

Class 6. Bisphenoidal class. Type, digonal holoaxial. 3 rectangular digonal axes of symmetry.

*Example*—Magnesium sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ .

Class 7. Pyramidal class. Type, di-digonal polar. A digonal axis and 2 mutually perpendicular planes of symmetry parallel to it.

*Example*—Ammonium magnesium phosphate,  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ .

Class 8. Bipyramidal or holohedral class. Type di-digonal equatorial. 3 rectangular digonal axes and 3 planes of symmetry perpendicular to each other.

*Example*—Potassium sulphate,  $\text{K}_2\text{SO}_4$ .

### IV. The Tetragonal System.

Characterised by 3 rectangular axes, of which two,  $a$  and  $b$ , are equal and are, therefore, both written as  $a$ , but the third, the vertical axis  $c$ , is different. Includes all crystals with one tetragonal axis of symmetry.

$$a : a : c = 1 : 1 : ? \quad \alpha = \beta = \gamma = 90^\circ.$$



Includes 7 classes.

Class 9. Pyramidal class. Type, tetragonal polar. One tetragonal axis of symmetry.  
*Example*—Wulfenite,  $\text{PbMoO}_4$ .

Class 10. Bisphenoidal class. Type, tetragonal alternating. One tetragonal axis and a plane of compound symmetry perpendicular to it.

*Example*—Only instance yet observed is the compound  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ .

Class 11. Trapezohedral class. Type, tetragonal holoaxial. One tetragonal axis and 4 digonal axes in the plane perpendicular to it.

*Example*—Strychnine sulphate,  $(\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2) \cdot \text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .

Class 12. Bipyramidal class. Type, tetragonal equatorial. One tetragonal axis and a plane of symmetry perpendicular to it.

*Example*—Scheelite,  $\text{CaWO}_4$ .

Class 13. Ditetragonal-pyramidal class. Type, ditetragonal polar. One tetragonal axis and 4 symmetry planes intersecting in it.

*Example*—Iodosuccinimide,  $\text{C}_4\text{H}_4\text{O}_2\text{NI}$ .

Class 14. Scalenohedral class. Type, ditetragonal alternating. One tetragonal axis and a plane of compound symmetry perpendicular to it; 2 rectangular digonal axes lying in the latter plane; 2 symmetry planes intersecting in the tetragonal axis and which bisect the angles of the two digonal axes.

*Example*—Potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ .

Class 15. Ditetragonal-bipyramidal or holohedral class. Type, ditetragonal equatorial. One tetragonal axis and 4 symmetry planes intersecting in it; also a symmetry plane and 4 digonal axes all perpendicular to the tetragonal axis.

*Example*—Zircon,  $\text{ZrSiO}_4$ .

#### V. The Trigonal System.

Characterised by 3 equal and equally inclined (otherwise than at  $90^\circ$ ) axes,  $a$ ,  $b$ ,  $c$ , all three written, therefore, as  $a$ . Includes all crystals with one trigonal axis of symmetry.

$$a : a : a = 1 : 1 : 1 \qquad \alpha = \beta = \gamma = ?$$

Includes 7 classes.

Class 16. Pyramidal class. Type, trigonal polar. One trigonal axis of symmetry.

*Example*—Sodium periodate,  $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ .

Class 17. Rhombohedral class. Type, hexagonal alternating. One trigonal axis of symmetry which is also a hexagonal axis of compound symmetry.

*Example*—Diopside,  $\text{CaH}_2\text{SiO}_4$ .

Class 18. Trapezohedral class. Type, trigonal holoaxial. One trigonal axis and 3 digonal axes in the plane perpendicular to it.

*Example*—Quartz,  $\text{SiO}_2$ .

Class 19. Bipyramidal class. Type, trigonal equatorial. One trigonal axis and a plane of symmetry perpendicular to it.

No example yet found.

Class 20. Ditrigonal-pyramidal class. Type, ditrigonal polar. One trigonal axis and 3 symmetry planes intersecting in it.

*Example*—Tourmaline,  $\text{H}_6\text{Na}_2\text{Fe}_4\text{B}_6\text{Al}_3\text{Si}_{12}\text{O}_{63}$ .

Class 21. Ditrigonal-scalenohedral class. Type, dihexagonal alternating. One trigonal axis and 3 symmetry planes intersecting in it; also 3 digonal axes in the plane perpendicular to the trigonal axis.

*Example*—Calcite,  $\text{CaCO}_3$ .

Class 22. Ditrigonal-bipyramidal or holohedral class. Type, ditrigonal equatorial. A trigonal axis and 3 symmetry planes intersecting in it; also a symmetry plane and 3 digonal axes all perpendicular to the trigonal axis.

*Example*—Silver hydrogen phosphate,  $\text{Ag}_2\text{HPO}_4$ .

VI. *The Hexagonal System.*

Characterised by 3 equal axes  $a, a, a$ , lying in the same plane and inclined at  $60^\circ$  to each other, and a fourth axis, the vertical axis  $c$ , perpendicular to them and unequal to them in length. This latter is a hexagonal axis of symmetry.

$$a : a : a : c = 1 : 1 : 1 : ? \quad a = \beta = 90^\circ, \gamma = 60^\circ.$$

Includes 5 classes.

Class 23. Pyramidal class. Type, hexagonal polar. One hexagonal axis of symmetry.

*Example*—Strontium antimonyl tartrate,  $\text{Sr}(\text{SbO})_2(\text{C}_4\text{H}_4\text{O}_6)_2$ .

Class 24. Trapezohedral class. Type, hexagonal holoaxial. One hexagonal axis and 6 digonal axes in the plane perpendicular to it.

*Example*—Barium antimonyl tartrate with pot. nitrate,  $(\text{C}_4\text{H}_4\text{O}_6)_2(\text{SbO})_2\text{Ba} \cdot \text{KNO}_3$ .

Class 25. Bipyramidal class. Type, hexagonal equatorial. One hexagonal axis and one plane of symmetry perpendicular to it.

*Example*—Apatite,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ .

Class 26. Dihexagonal-pyramidal class. Type, dihexagonal polar. One hexagonal axis and 6 symmetry planes intersecting in it.

*Example*—Greenockite,  $\text{CdS}$ .

Class 27. Dihexagonal-bipyramidal or holohedral class. Type, dihexagonal equatorial. One hexagonal axis and 6 symmetry planes intersecting in it; also a symmetry plane and 6 digonal axes perpendicular to the hexagonal axis.

*Example*—Beryl,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ .

VII. *The Cubic System.*

Characterised by 3 equal rectangular axes,  $a, b, c$ , all three written, therefore, as  $a$ .

$$a : a : a = 1 : 1 : 1 \quad a = \beta = \gamma = 90^\circ.$$

Includes the 5 classes with 3 rectangular digonal or tetragonal axes of symmetry and 4 trigonal axes of symmetry.

Class 28. Tetrahedral-pentagonal-dodecahedral class. Type, tesseral polar. 3 equal rectangular digonal axes and 4 equal trigonal axes equally inclined to the others.

*Example*—Barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ .

Class 29. Pentagonal-icositetrahedral class. Type, tesseral holoaxial. 3 equal rectangular tetragonal axes; 4 trigonal axes equally inclined to the tetragonal ones; also 6 digonal axes each bisecting the angle between two of the tetragonal axes.

*Example*—Cuprite,  $\text{Cu}_2\text{O}$ .

Class 30. Dyakis-dodecahedral class. Type, tesseral central. 3 equal rectangular digonal axes and 4 equal trigonal axes equally inclined to them; also 3 planes of symmetry perpendicular to the digonal axes.

*Example*—Pyrites,  $\text{FeS}_2$ .

Class 31. Hexakis-tetrahedral class. Type, ditesseral polar. 3 equal rectangular digonal axes and 4 equal trigonal axes equally inclined to them; also 6 symmetry planes bisecting the angles of the symmetry planes of class 30.

*Example*—Tetrahedrite,  $\text{Cu}_3\text{SbS}_3$ .

Class 32. Hexakis-octahedral or holohedral class. Type, ditesseral central. 3 equal rectangular tetragonal symmetry axes, 4 equal trigonal axes equally inclined to them, and 6 digonal axes each bisecting the angle between two of the tetragonal axes; also 3 symmetry planes perpendicular to the tetragonal axes, and 6 symmetry planes bisecting the angles between the first 3 symmetry planes. This is the highest possible combination of elements of symmetry.

*Example*—Fluorspar,  $\text{CaF}_2$ .

## CHAPTER X

### THE CUBIC SYSTEM, ALSO CALLED REGULAR OR TESSERAL

**Three equal rectangular crystallographic axes. Symmetry elements characteristic of system: 3 rectangular digonal or tetragonal axes of symmetry and 4 trigonal axes of symmetry.**

THIS highest system of crystal symmetry consists of 5 classes, the lowest of which possesses the essential minimum elements of symmetry mentioned above, namely, 4 trigonal axes and 3 digonal axes of symmetry, the latter arranged at right angles to each other and coincident with the crystallographic axes. These elements of symmetry, and the repetitions of the general pole ( $hkl$ ) to which by their operation they give rise, are shown in the stereographic projection Fig. 79. The poles

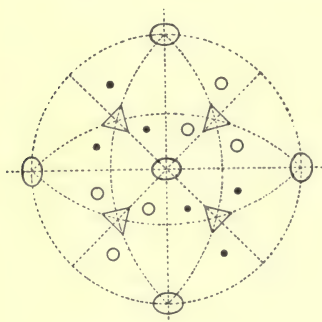


FIG. 79.—Class 28.

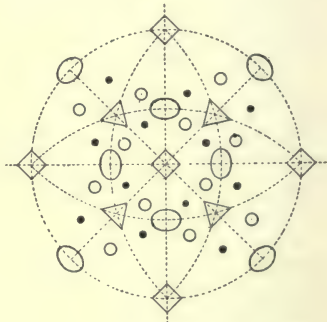


FIG. 80.—Class 29.

or points of emergence of the trigonal axes are indicated by small triangles, and the poles of the digonal axes by little ellipses. The facial poles in the upper hemisphere above the plane of the paper are indicated by dots as usual, and those of the lower hemisphere by miniature rings. If the digonal axes be replaced by tetragonal ones, the poles of emergence of which from the sphere may be indicated by little squares, we have the second of the five classes, the projection of which is given in Fig. 80, the figure being then seen to be symmetrical also about 6 new digonal axes arranged diagonally. In both figures the



crystallographic axes are indicated by the two rectangular diameters parallel to the edges of the page, and by the centre, which represents in the projection the diameter of the sphere perpendicular to the page.

In the tetragonal system to be considered in Chapter XII., which most closely resembles the cubic system, the characteristic of the system is a single tetragonal axis. Similarly, the trigonal system described in Chapter XXII. possesses a single trigonal axis, and the hexagonal system considered in Chapter XX. is endowed with a single hexagonal axis of symmetry. It is the possession of this single vertical axis of trigonal, tetragonal, or hexagonal symmetry that unites the three systems named after these axes in the optically uniaxial class of crystals, conferring as it does special optical properties in the vertical direction. But the cubic system is unique in possessing more than a single axis of higher symmetry than digonal. For the degree of symmetry goes up by leaps and bounds the moment we introduce more than one such axis of higher symmetry, so that even the lowest class of the cubic system becomes automatically possessed of four trigonal axes by the mere act of attempting to add a second one; and the lowest class but one comes into possession of three tetragonal axes when we attempt to add one more to the single one of the tetragonal system.

The lowest class of the cubic system, class 28, is distinguished, therefore, by having more than one trigonal axis of symmetry, a single trigonal axis being the characteristic of the trigonal system. The addition of one more can only be effected in such a manner as to produce by the operation of the pair a solid which is really symmetrical about four such trigonal axes. Four, therefore, is the smallest number of trigonal axes that we can have in operation, the moment we step above a single trigonal axis. These four are the normals to the regular octahedron or tetrahedron faces, their angle of mutual intersection being the same as the crystallographic angle over the edges of the tetrahedron,  $109^{\circ} 28'$ . The poles of emergence of these four trigonal axes are indicated in Fig. 79 by the little triangles, occupying the positions of the octahedron poles. If we take any general facial pole ( $hkl$ ) in the upper right front octant, rotation for  $120^{\circ}$  and  $240^{\circ}$  round the trigonal axis emerging in this octant will cause the facial pole to be repeated twice more at  $120^{\circ}$  intervals in the octant, making three facial poles altogether in that octant, as indicated by the three dots. If now we rotate the whole for  $120^{\circ}$  about an adjacent trigonal axis, say that emerging in the left front octant, the three poles of the upper right front octant become coincident with three analogous ones in the lower left front octant, as indicated by the three little rings. This can be readily verified with a model of an octahedron (Fig. 85), through the centres of the four pairs of parallel faces of which long needles have been perpendicularly inserted; for on rotating the octahedron for  $120^{\circ}$ , that is, until the original aspect is restored, about the needle corresponding to the trigonal axis in question, the upper right front face will be seen to become the lower left front one.

Similarly, a further rotation for  $120^\circ$  about either this same trigonal axis or the trigonal axis emerging in the upper right back octant reproduces the original three dotted poles in the upper left back octant, as again indicated by three dots, and rotation for  $120^\circ$  in the inverse way, or  $240^\circ$  in the same way, about the fourth trigonal axis emerging in the upper left back octant will repeat the first three dotted poles as ring-poles in the lower right back octant. All these effects can be verified in the same manner by the rotation of the octahedron about the corresponding needles.

The total effect is thus to produce a 12-faced solid, the tetrahedral pentagonal dodecahedron (Figs. 128 and 129), which has two sets, of three faces each, in each hemisphere, alternately arranged in the two hemispheres as regards octants, as will be clear from the projection (Fig. 79). It will be obvious, on inspection of this figure, that there is further symmetry about three mutually rectangular digonal axes, which are identical with the axes of the cube. For, half a revolution about any one of the three will end with the figure being of precisely the same aspect as it was before the rotation.

Class 29 is produced by adding to these symmetry elements of class 28 six more digonal axes parallel to the normals to the faces of the rhombic dodecahedron (a well-known solid which will be fully described a few pages hence and illustrated in Fig. 86), that is, bisecting the angles between the cube normals. Fig. 80 shows the conditions, and it will be observed that the six new axes of symmetry occupy the diagonal diameters of the sphere. Moreover, it will be observed that the three old digonal axes are now indicated by squares, for the figure is such that rotation for  $90^\circ$  about these cube normals recovers the same aspect again, so that these axes are no longer merely digonal but tetragonal. Thus here we jump, as it were, from the single tetragonal axis of the tetragonal system to a class of symmetry possessing three such axes. The faces of the solid are double the number of those of class 28, being 24, every pole of class 28 having in class 29 a fellow in the other hemisphere, by rotation for  $180^\circ$  about one of the six new digonal axes. It is the pentagonal icositetrahedron (Figs. 124 and 125).

This is the maximum combination of symmetry axes possible to a crystal, and any further advance in symmetry must be brought about by the addition of planes of symmetry. We then obtain three further classes, 30, 31, and 32.

Class 30, represented in stereographic projection by Fig. 81, is produced by adding to class 28 three symmetry planes parallel to the faces of the cube, indicated by the primitive circle and the two diameters parallel to the edges of the page being drawn in continuous lines.

By repetition about these three planes of symmetry the 12 facial poles of

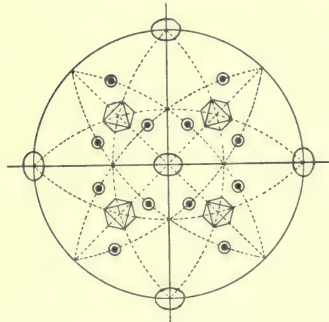


FIG. 81.—Class 30.

Fig. 79 become doubled, each one having a parallel fellow added at the other side of the centre, so that all the facial-polar positions are occupied by ringed dots. The solid produced is the dyakis dodecahedron (Fig. 115). A further effect of the addition of the three planes of symmetry is to render the four trigonal axes also hexagonal axes of compound or reflective symmetry, and the little triangles are surrounded by hexagons to indicate the fact.

Class 31 is formed by adding to the symmetry elements of class 28 six planes of symmetry parallel to the faces of the rhombic dodecahedron, that is, planes at  $45^\circ$  to the cube faces, the angles of intersection of which they consequently bisect. They are indicated in Fig. 82 by the two diagonal diameters and four circular arcs being drawn in continuous lines. The effect is to add also 12 more faces to the 12 of class 28, but this time by adding three more facial poles to the three already present in each octant, in the case of the four octants occupied by poles in class 28, pro-

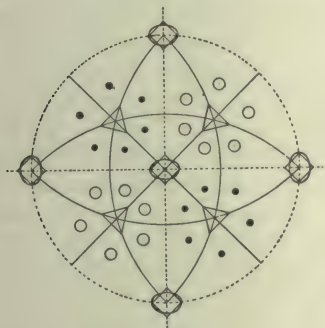


FIG. 82.—Class 31.

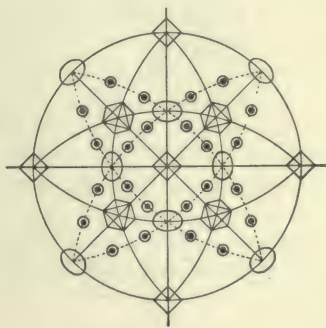


FIG. 83.—Class 32.

ducing as the solid the hexakis tetrahedron (Fig. 107). Moreover, the three cube normals become tetragonal axes of compound symmetry, hence the ellipses indicating their points of emergence from the sphere are interpenetrated by squares in Fig. 82.

Finally, by combining all the elements of symmetry present in all the other four classes, or, which is the same thing, those of classes 29, 30, and 31, we arrive at the class of highest possible crystal symmetry, class 32, possessing 22 elements of symmetry, indicated in stereographic projection by Fig. 83. In this class we have present the **three tetragonal axes of symmetry**, coincident with the crystallographic axes, the **four trigonal axes of symmetry**, which are also hexagonal axes of compound symmetry, and the **six digonal axes of symmetry**, bisecting the angles of intersection of the tetragonal ones; also **three rectangular planes of symmetry** parallel to the faces of the cube and intersecting in the crystallographic axes and the three tetragonal axes, and **six diagonal planes of symmetry** bisecting the angles of the cube planes, that is, parallel to the faces of the rhombic dodecahedron, intersecting each other in pairs in the crystallographic axes, and intersecting the 3 cubic planes of symmetry in the six digonal



axes. The number of faces and of the corresponding facial poles is now again doubled to 48, the solid being the hexakis octahedron (Fig. 96), there being 6 poles in each of the 8 octants, those of the upper hemisphere immediately above those of the lower, so that we have 24 dots each surrounded by a ring.

The general form  $\{hkl\}$  of each of these 5 classes, the poles of which are shown on the 5 stereographic projections, Figs. 79 to 83, consists of faces having the same index numbers, when the 3 cube planes are taken as axial planes and the edges of the cube, or, which is the same thing, the cube normals are taken as the axial directions; it is assumed also that the regular octahedron is the parametral form, its faces being perpendicular to the trigonal axes of symmetry, so that the axial lengths are equal. The order of these same index numbers of the general form of course varies for the different faces (three or six) in the same octant, and the signs vary for the different octants.

Having thus traced the evolution of the 5 classes of the cubic system, we are in a favourable position for considering these classes in detail, and studying the nature of the forms possible to each of them.

The cubic system is unique in that the whole of the interfacial angles of the crystals belonging to it are definitely fixed by the symmetry, and are therefore invariable. Not merely does this refer to such angles as are  $90^\circ$ ,  $60^\circ$ ,  $45^\circ$ , and  $30^\circ$ , but to all the interfacial angles whatsoever, to those of the rarer forms equally as well as to those of the primary and other common forms. The absolute values of the angles of each form, correct to one minute of arc, will be stated in the course of the description of the various forms which will now be given.

### HOLOHEDRAL FORMS OF THE CUBIC SYSTEM.

*Class 32.—Class of Highest Crystal Symmetry. Hexakis-Octahedral Class. Holohedral Class of the Cubic System. Type, Ditesseral Central.*

This holohedral<sup>1</sup> class of the cubic system of crystals, the 22 elements of symmetry of which have just been enumerated, and which together represent the maximum amount of symmetry developed by crystals, comprises seven simple forms, each being a well-known geometrical solid. They are, respectively, the cube (the axial-plane form), octahedron (the parametral form), the rhombic dodecahedron (with faces parallel to the diagonal planes of symmetry), the hexakis octahedron (the general form  $\{hkl\}$ ), the icositetrahedron, the triakis octahedron, and the tetrakis hexahedron.

(1) The fundamental form, the three pairs of faces of which are chosen as the axial planes intersecting each other at right angles (exactly  $90^\circ 0'$ ), is the cube or regular hexahedron, Fig. 84. The normals to its faces, parallel to its edges, are both the three crystallographic rectangular equal axes and the three tetragonal symmetry axes. The form symbol is  $\{100\}$ , for each pair of faces cuts one of the crystallographic axes only, and is parallel to the other two, so that the intercepts upon those two are

<sup>1</sup> It is convenient to retain the term "holohedral" to distinguish the class of crystals exhibiting the full symmetry of a system.

$\infty$  and the indices consequently 0. As regards the six separate sets of facial indices, those of the front face meeting the axis  $a$  are identical with those of the form, namely (100). The indices of the parallel face behind are ( $\bar{1}00$ ). Those of the two faces meeting the axis  $b$  right and left of the centre are respectively (010) and (0 $\bar{1}$ 0), while those of the top and bottom horizontal faces meeting the axis  $c$  are respectively (001) and (00 $\bar{1}$ ). All the faces being of similar value as regards the symmetry, and this being of such a perfect character, it is immaterial which of the three pairs of faces are regarded as the horizontal ones, and which as the front and back ones. Simple cubes are frequently found of rock salt, sodium chloride NaCl, fluor-spar, calcium fluoride  $\text{CaF}_2$ , and galena, lead sulphide PbS.

(2) The parametral form is the **octahedron** {111}, shown in Fig. 85. Each of its eight faces forms an equilateral triangle. All its edges are similar, and the angle

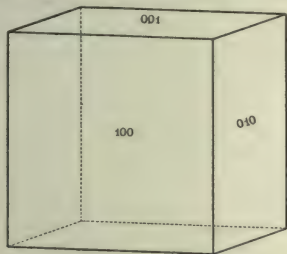


FIG. 84.—The Cube.

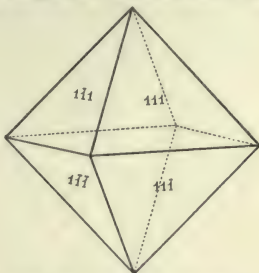


FIG. 85.—The Octahedron.

across any one of them, that is, the angle between the normals to any two adjacent faces, is  $70^\circ 31' 44''$ . The four normals are the four trigonal symmetry axes of the cubic system; the twelve equal edges lie (four in each, making a square) in the three axial planes, the three principal planes of symmetry; and each parallel pair of edges is perpendicular to one of the six digonal axes of symmetry of the system, and parallel to one of the six diagonal planes of symmetry. The eight faces have the following symbols: the face in the upper right front octant (111), that in the upper left front octant ( $\bar{1}11$ ), that in the upper left back ( $\bar{1}\bar{1}1$ ), that in the upper right back ( $\bar{1}1\bar{1}$ ), that in the lower right front ( $11\bar{1}$ ), that in the lower left front ( $\bar{1}\bar{1}\bar{1}$ ), that in the lower left back ( $\bar{1}\bar{1}\bar{1}$ ), and that in the lower right back octant ( $\bar{1}\bar{1}\bar{1}$ ). The six solid angles are all similar, and are formed by the meeting of four equal edges at angles of  $60^\circ$ .

Spinel,<sup>1</sup> aluminate of magnesia,  $\text{MgAl}_2\text{O}_4$ , and magnetite,  $\text{Fe}_3\text{O}_4$  (probably ferrous ferrate  $\text{Fe}''\text{Fe}_2'''\text{O}_4$ ), are examples of minerals crystallising in octahedra.

(3) The next simplest form is the **rhombic dodecahedron** {110}, which is represented in Fig. 86. As its name implies, it is composed of twelve congruent faces of rhombic shape, each being a regular rhombus, the plane angles of which are equal to the octahedron angle,  $70^\circ 31' 44''$ , and its supplement,  $109^\circ 28' 16''$ . Each face is inclined to two of the crystallographic axes only, and is parallel to the third axis. It meets the two axes in question at  $45^\circ$ , thus cutting off equal lengths from them. Hence the intercepts are always  $\infty$  for one axis and equal definite lengths along the two others, so that the indices of each face are composed of one cipher and two ones. The four faces parallel to the vertical axis  $c$  have the indices respectively

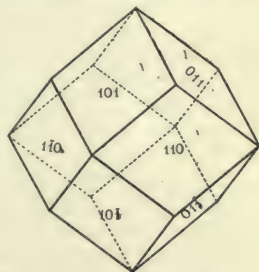


FIG. 86.—The Rhombic Dodecahedron.

<sup>1</sup> For the structure of spinel as revealed by X-rays see Chapter XXXIII.

(110) right front, ( $\bar{1}\bar{1}0$ ) left front, ( $\bar{1}\bar{1}0$ ) left back, and ( $\bar{1}\bar{1}0$ ) right back. The four faces parallel to the back-to-front  $a$  axis are respectively (011) right upper, and (0 $\bar{1}\bar{1}$ ) right lower; and (0 $\bar{1}\bar{1}$ ) left upper, and (011) left lower. The remaining four faces parallel to the lateral  $b$  axis are (101) front upper, and (10 $\bar{1}$ ) front lower; and ( $\bar{1}01$ ) back upper, and ( $\bar{1}0\bar{1}$ ) back lower. The angle between the normals to every adjacent pair of faces is  $60^\circ$ , while the angles between the four faces parallel to any one and the same axis are all  $90^\circ$ . The most interesting fact about the rhombic dodecahedron, however, is that its six pairs of parallel faces are parallel to the six diagonal planes of symmetry of the cubic system, so that it may be said that the dodecahedron is symmetrical to its own faces. Each pair of faces is consequently also normal to one of the six digonal axes of the system. Another interesting property is that, like the cube, an indefinite number of rhombic dodecahedra will pack together in space without leaving any interstices, provided all are of the same size. The octahedron will not do so; but a combination of the cube and octahedron, in which the cube corners (solid angles) are truncated by octahedron faces to the extent that

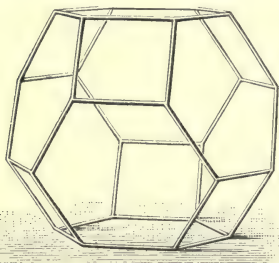


FIG 87.—The Tetrakaidekahedron of Lord Kelvin.

tetrakaidekahedron which was exhibited by Lord Kelvin in his Boyle Lecture at Oxford in the year 1893 is given in Fig. 87.

The solid angles of the rhombic dodecahedron are of two kinds, namely, six equiangular four-faced quoins and eight equiangular three-faced ones, the points of the former being at the ends of the three principal axes, and those of the latter occupying the middle of the octants and lying on the four trigonal axes. These latter three-faced quoins are consequently replaced or *modified* or *truncated* by small octahedron faces, when such are developed to a subsidiary extent in a combination of the two forms; and the four-faced quoins are replaced by little faces of the cube, when this form is developed to a subsidiary extent on a crystal which develops the rhombic dodecahedron as the principal, habit determining, form. These facts will be rendered clear by Figs. 90 and 91, to be described directly in dealing with the combinations. Garnet,  $R_3R_2'''(\text{SiO}_4)_3$ , is very generally found in rhombic dodecahedra.

The three forms now dealt with, the cube, octahedron, and rhombic dodecahedron, have one property of great importance in common, which distinguishes them from the other four holohedral forms of the cubic system, namely, that the symmetry of the system only permits of there being one cube, one octahedron, and one rhombic dodecahedron; whereas several distinct representatives of the other four forms are possible and are actually observed in practice.

Before passing on to the consideration of the other four holohedral forms of the cubic system, with their variable character, it will, therefore, be well to refer to the **combinations** of the three permanent forms

<sup>1</sup> The Robert Boyle Lecture, "The Molecular Tactics of a Crystal," Oxford, 1893.



now studied. Two such combinations of all three forms are shown in Figs. 88 and 89, the cube faces being marked *c*, the octahedron faces *o*, and the rhombic dodecahedron faces *d*. Starting from the cube as the primitive form, it will be observed that the octahedron truncates (replaces symmetrically) the corners of the cube, while the rhombic dodecahedron truncates its edges. A crystal showing all three forms among which the cube predominates, as represented in Fig. 88, appears with both the corners and the edges of the latter truncated; while a combination of all three such as is shown in Fig. 89, in which the octahedron predominates, appears with all the solid octahedral angles truncated by small cube faces, and all the octahedral edges truncated

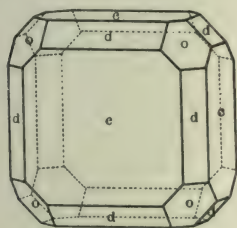


FIG. 88.

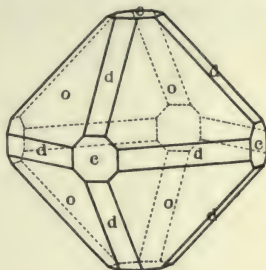


FIG. 89.

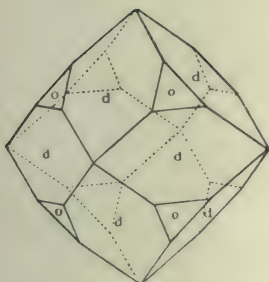


FIG. 90.

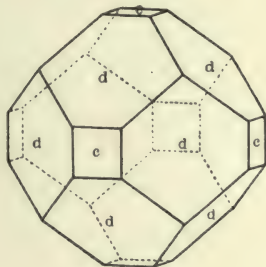


FIG. 91.

Combinations of Cube, Octahedron, and Rhombic Dodecahedron.

by narrow faces of the dodecahedron. These modifications of edges and solid angles, by a plane making equal angles with the adjacent faces, afford excellent examples of "**truncation**." The two further combinations shown in Figs. 90 and 91 indicate the effect, already referred to on page 146, of slightly modifying the rhombic dodecahedron by small faces of the octahedron and cube respectively.

Most crystals exhibit more than one form, and combinations of these three simple forms are very common, and indeed some of the other four holohedral forms of the cubic system are often present with them. A practical example, a garnet crystal, showing faces of the rhombic dodecahedron and the icositetrahedron, will be described in the next chapter and its measurement followed.

Before leaving the consideration of these three important simple forms it is advisable that their stereographic projection should be given and thoroughly understood, as a necessary basis of operations for practical work on cubic crystals. It is given in Fig. 92. The poles of the cube faces are marked *c*, those of the octahedron *o*, and those of the rhombic dodecahedron *d*. The primitive circle is is, of course, the plane of the crystallographic axes *a* and *b*, the third axis *c* perpendicular to the plane of the paper being represented by the pole in the centre. This pole is also that of the pair of parallel horizontal cube faces, the poles of the two pairs of vertical faces being at the extremities of the axes *a* and *b* on the primitive circle.

The poles of the rhombic dodecahedron are next found as follows. Four of them are situated at the points midway between, that is,  $45^\circ$  from, the poles of the cube on the primitive circle. The

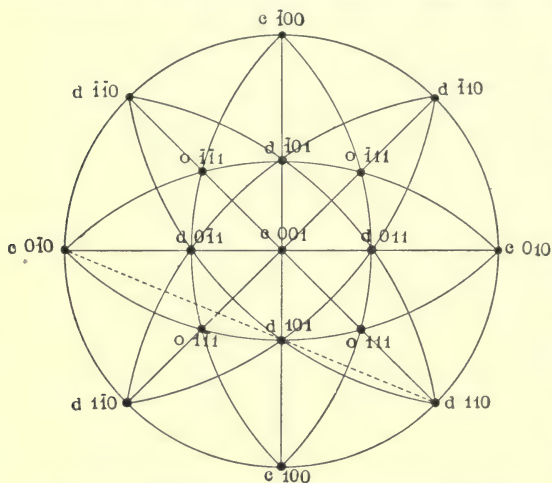


FIG. 92.—Stereographic Projection of Cube, Octahedron, and Rhombic Dodecahedron.

remaining eight are situated at the similar  $45^\circ$  positions on the great circles the projections of which are the diameters which represent also the axes *a* and *b* and join the poles of the cube faces. To find the projections of the dodecahedron poles on these diameters, one operation only is sufficient, and it will incidentally also afford us the means of locating the poles of the octahedron. The operation required is an application of the rule given on page 97 in Chapter VI, namely, to find first the pole of the zone, and then to join it to a point marked off along the primitive circle at the required angle (here  $45^\circ$ ) from the end of the diameter representing the zone. To find, for instance, the pole (101) on the zone circle represented by the vertical diameter:—The pole of the zone circle may be either extremity of the horizontal diameter on the primitive circle. Let it be the left extremity which is taken, coincident with the facial pole (010) of the cube. The  $45^\circ$  points have already been marked off along the primitive circle in finding the poles of the dodecahedron which lie on that circle; we have, therefore, merely to join the pole (010) to the pole of one of the two dodecahedron faces already found in the right primitive semicircle, say (110). The line thus drawn cuts the vertical diameter, representing the zone circle on which we desire to find one of the dodecahedron poles, at the particular dodecahedron pole required, (101). From the centre, with the distance between the poles (001) and (101) as radius, we have only to mark off the three other similar positions, one ( $\bar{1}01$ ) above the centre along the same zone circle, and the other two (011) and (0 $\bar{1}$ 1) at the symmetrical right and left positions on the zone circle represented by the horizontal diameter. Each of the four positions thus found as the projections of dodecahedron faces represents two faces, one in the upper hemisphere, marked by a dot, and another vertically beneath it in the lower

hemisphere, which might, if desired, be marked by a miniature ring surrounding the dot, and which has similar indices except that the  $c$  index is negative. If we now draw circular arcs through these four poles just found and the poles of both cube and dodecahedron on the primitive circle, so as to connect up all the possible zones, as shown in Fig. 92, we find that the arcs terminating at the cube poles intersect each other in pairs on the diagonal diameters, and these points of intersection of three zones are the poles of the octahedron faces. This can be immediately proved by calculating the angle between any two of these octahedron poles on the projection, say between  $(111)$  and  $(\bar{1}\bar{1}\bar{1})$ , when it will be found to be the accepted octahedron angle. The calculation is very simple, if we consider the half angle  $(111) : (101)$ . For in the triangle made by this arc with the central pole  $(001)$  the angle at  $(001)$  is  $45^\circ$ , the arc  $(001) : (101)$  is also  $45^\circ$ , and the angle at  $(101)$  is a right angle. Constructing a Napierian diagram, as shown in Fig. 93, we have by Napier's rules :

$$\cos o = \sin 45^\circ \cos 45^\circ ; \sin do = \cot o \tan 45^\circ.$$

$$\begin{aligned} &= \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} = \frac{1}{2} & \text{Log. cot } 60^\circ & \bar{1}.76144 \\ & & \text{Log. tan } 45^\circ & 0.00000 \\ & \cos o = 60^\circ & \text{Log. sin } do & \bar{1}.76144 \\ & & do = 35^\circ 15.9' & \end{aligned}$$

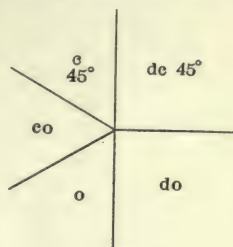


FIG. 93.

It will be shown directly to be instructive to know the value of this angle at  $o$ . But if we had not needed it we might have calculated the angle  $do$  more directly from the Napierian diagram thus :

$$\sin 45^\circ = \tan do \cot 45^\circ, \text{ or } \tan do = \sin 45^\circ \tan 45^\circ.$$

$$\begin{aligned} &\text{Log. sin } 45^\circ \quad \bar{1}.84949 \\ &\text{Log. tan } 45^\circ \quad 0.00000 \\ &\text{Log. tan } do \quad \bar{1}.84949 \\ &do = 35^\circ 15.9' \end{aligned}$$

Hence the whole arc  $oo$ ,  $(111) : (\bar{1}\bar{1}\bar{1})$ , twice  $do$ , is  $70^\circ 31.8'$ , which is the angle between the normals to any two adjacent octahedron faces.

The angular value of the arc  $co$ ,  $(001) : (111)$ , may also be found from the same triangle :

$$\begin{aligned} \cos co &= \cos do \cos dc \\ &= \cos 35^\circ 15.9' \cos 45^\circ \\ \text{Log. cos } 35^\circ 15.9' & \bar{1}.91195 \\ \text{Log. cos } 45^\circ & \bar{1}.84949 \\ \text{Log. cos } co & \bar{1}.76144 \\ co &= 54^\circ 44.1' \end{aligned}$$

Thus the arc  $c = (001) : o = (111)$  is  $54^\circ 44.1'$ , the half supplement of the octahedron angle. It is also the complement of the angle  $do$  just found, for  $do = (110) : (111)$  is the same as the latter,  $(101) : (111)$ , as is proved by this calculation. The angle at  $o = (111)$  between the two arcs just calculated has also been shown above to be  $60^\circ$ . As each of these arcs represents an edge, the arc  $co$  corresponding to that formed by the truncation of the upper right front octahedron face by the top cube face, or the parallel right front horizontal edge of the octahedron, and the arc  $oo$  to the front upper edge of the octahedron, this angle of  $60^\circ$  is the angle between two adjacent edges of the octahedron face, that is, the face is an equilateral triangle.

Hence we now know the whole of the angular dimensions of every part of the stereographic projection, both interpoles (interfacial) arcs and interzonal angles.



As we now thoroughly understand, therefore, the stereographic projection of these simple holohedral forms of the cubic system, we are in a more favourable position to appreciate the expression of the symmetry of this highest class 32 of the cubic system, as given in Fig. 94, which is Fig. 83 repeated here for convenience of reference.

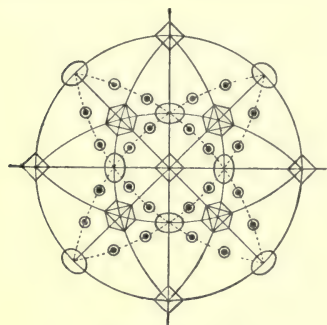


FIG. 94.—Class 32.

surrounded by hexagons, and the 6 digonal axes are marked by elliptical rings. The 3 tetragonal poles are identical with those of the cube faces, the 4 trigonal with those of the octahedral faces, and the 6 digonal with those of the rhombic dodecahedron. The small ringed dots also given on the projection are the poles of the general holohedral form  $\{hkl\}$  of the system, the 48-faced hexakis octahedron (Fig. 96), the dot representing the face on the upper hemisphere and the ring that on the lower one. The actual hexakis octahedron shown is the commonest one  $\{321\}$ . This form is the next to be con-

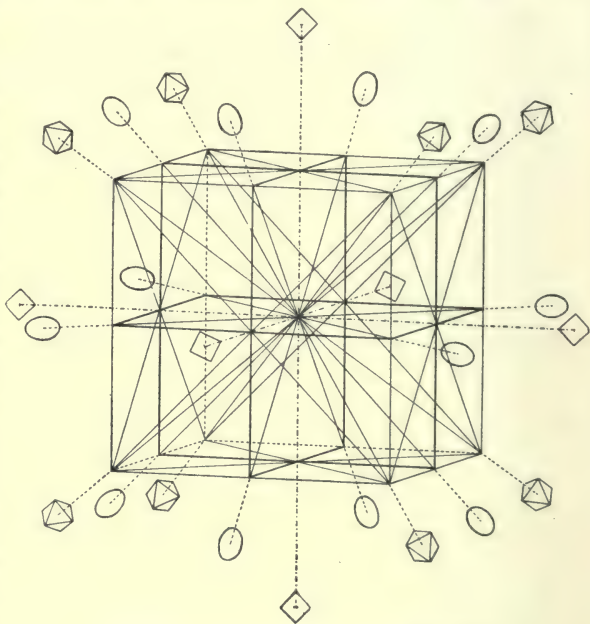


FIG. 95.—Axes and Planes of Cubic Symmetry.

sidered, but before passing to it reference must be made to the attempt in Fig. 95 to exhibit the axes and planes of symmetry of the cubic system in perspective about a cube. Owing to their number, it is not easy to do so with great clearness in a single diagram (except as just shown, in stereographic projection), but by marking the three types of symmetry

axes with the Gadolin symbols as in the case of the stereographic projection, and by emphasising the three rectangular planes of symmetry coincident with the crystallographic axial planes by means of thicker lines, to distinguish them from the six diagonal planes of symmetry drawn in thin lines, the elements of the perfect symmetry of class 32 of the cubic system may be grasped. A comparison with Fig. 94 will be found very helpful, and the two figures are placed near to each other for the purpose of facilitating such a comparison.

The high order of symmetry which is displayed in the cubic system will be very apparent from this diagram, Fig. 95. For, as explained on page 143, there are no less than 22 elements of symmetry present in class 32.

It is of historic interest that the perfection of symmetry inherent in the cube was clearly recognised by the ancient Greek geometricians, a fact which is reflected in the adoption by the Greeks of the cube as the general emblem of perfection. Hence it is that in the description of the Holy City, given in the Book of the Revelation of St. John the Divine,<sup>1</sup> its ideal perfection is symbolised by the properties of the cube. For we read (as translated from the original Greek) "the city lieth foursquare," and "the length and the breadth and the height of it are equal."

(4) We now come to the consideration of the general holohedral form of the system above referred to,  $\{hkl\}$ , the **hexakis octahedron**. As its name implies, it may be considered as an octahedron each face of which is replaced by 6 others, thus producing a solid of 48 faces. Or it may be more generally regarded as the figure demanded by the full symmetry of the cubic system when any one face ( $hkl$ ) is assumed to exist. That is, any face ( $hkl$ ), cutting off unequal intercepts from the three axes, requires to be associated with 47 others in order to fulfil the conditions of full cubic symmetry. The hexakis octahedron  $\{321\}$  is shown in Fig. 96.

Each facial pole occupies one of the continuous-line triangles of the stereographic projection shown in Fig. 94. The faces themselves, when all are equally developed, are shaped as scalene triangles, the edges of intersection which form these triangles lying in the various planes of symmetry. There are thus three kinds of edges, the triangles being all similar, and there are consequently in general three correspondingly different sets of angles, over these edges, between the normals to adjacent faces. These three angles as measured goniometrically are given below for the two commonest representatives of the form,  $\{321\}$  and  $\{421\}$ .

	Angle over Longest Edge.	Angle over Shortest Edge.	Angle over Medium Edge.
For {321} .	21° 47'	21° 47'	31° 0'
For {421} .	17 45	35 57	25 13

The edges of medium length lie in the three axial planes of symmetry, and the sections of the crystal made by these planes are octagons of equal edges but not regular, the angles being of two alternating kinds.

In the representation of the form {321} in Fig. 96 the indices of the various faces on the front hemisphere are inserted, in order to indicate the character of the permuta-

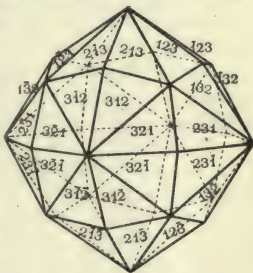


FIG. 96.—The Hexakis Octahedron  $\{321\}$ .

<sup>1</sup> "The Revelation of St. John the Divine," chap. xxi., verse 16.

tions of the three numbers which occur. This particular hexakis octahedron has the peculiarity that, as indicated by the above angular values, the angles over two kinds of edges, the longest and the shortest, are equal.

The solid angles are of three kinds, six eight-faced the points of which are on the crystallographic axes, eight six-faced meeting in the four trigonal axes, and twelve four-faced meeting in the 6 digonal axes of symmetry.

All faces having three unequal indices belong to this form.

The hexakis octahedron is scarcely known in its simple form, for, although many diamonds<sup>1</sup> appear to be hexakis octahedra, their faces are usually so rounded

that it is not possible to verify the presence of the form by measurement. But it is often found in combination with other of the holohedral forms of the cubic system, for instance in spinel and garnet. Fig. 97 shows a garnet exhibiting a combination of the hexakis octahedron  $\{321\}$ , the faces of which are marked with the letter  $h$ , with the rhombic dodecahedron  $\{110\}$ , the faces of which are marked  $d$ . The edges  $hd$  are parallel to the longer edges  $hh$  of the hexakis octahedron  $\{321\}$ , the rhombic dodecahedron faces replacing the four-faced solid angles of this particular hexakis octahedron in a symmetrical manner; the poles of  $\{321\}$  are consequently situated on the dodecahedral arc zones, those shown in dotted lines in Fig. 94, that is, the

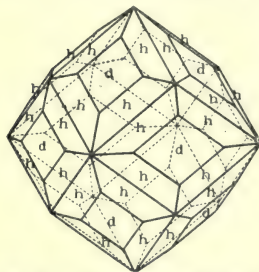


FIG. 97.—Combination of Hexakis Octahedron and Rhombic Dodecahedron.

faces of  $\{321\}$  belong to the dodecahedral zones.

(5) When two of the index numbers in the symbol  $(hkl)$  become equal the number of permutations of the indices, and therefore the number of faces comprising the form, is reduced to half, namely, 24. There are two new varieties of simple forms thus produced, in which the two equal indices are respectively less or greater than the third. The former case is that of the icositetrahedron, the latter that of the triakis octahedron. The indices of these two forms are usually written as  $\{hkk\}$  and  $\{hhl\}$ ,  $h$  being greater than either  $k$  or  $l$ .

The **icositetrahedron**, the commonest representative of which,  $\{211\}$ , is shown in Fig. 98, possesses only two kinds of edges, half being of each kind. There are 24 longer edges lying in the axial planes, of which every four make up a solid angle the point of which is on the crystallographic axis, and 24 shorter edges lying in the 6 digonal planes of symmetry, of which the eight sets of three each meet in a solid angle on the trigonal axes of symmetry. The faces also group themselves into six other sets of four each, two longer and two shorter edges in each set, meeting in the digonal axes of symmetry. The icositetrahedron may be regarded as derived from the hexakis octahedron by the fusion into a single face of the two faces meeting in each of the longest of the three kinds of edges possessed by that 48-faced solid.

Leucite,  $\text{KAl}(\text{SiO}_3)_2$ , and garnet exhibit characteristically the icositetrahedron  $\{211\}$ . An icositetrahedral crystal of garnet showing also faces of the rhombic dodecahedron will be fully worked through as a practical goniometrical example in the next chapter.

The angles met with in measurements on the goniometer, between the normals to adjacent faces of the two commonest icositetrahedra, are as under :

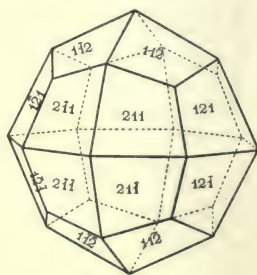


FIG. 98.

The Icositetrahedron  $\{211\}$ .  
The Icositetrahedron

<sup>1</sup> For the structure of the diamond as revealed by X-rays, and its interesting bearing on the chemistry of carbon, see Chapter XXXIII.



	Over the Longer Edges.	Over the Shorter Edges.
For {211} . . .	48° 11'	33° 33'
For {311} . . .	35 6	50 29

(6) The **triakis octahedron**, of which the forms {221} and {331} are those most commonly met with, may be regarded as an octahedron every face of which is replaced by a low three-faced pyramid, or a hexakis octahedron the shortest edges of which have disappeared, the two faces on each side of each such short edge having become one face. Its faces are all isosceles triangles, the 12 longer edges of which all lie in the 3 principal planes of symmetry, four in each, and are actually parallel to (or they may be regarded as identical with) the edges of the octahedron. The form {221} is shown in Fig. 99. The angle over these edges, between the normals to each pair of faces forming the edge by their intersection, for the form {221}, is 38° 57', and for the form {331}, 26° 32'. The other 24 shorter edges intersect in 8 three-faced solid angles, the points of which lie on the axes of trigonal symmetry. The angle over these shorter edges, between the normals to the adjacent faces forming the edge in each case, is 27° 16' for the form {221} and 37° 52' for the form {331}. The triakis octahedron shows also six eight-faced solid angles, the quoins of which are formed by four longer and four shorter edges alternately arranged, and the points of which are identical with the apices of the octahedron. The diamond sometimes exhibits the form {221}.

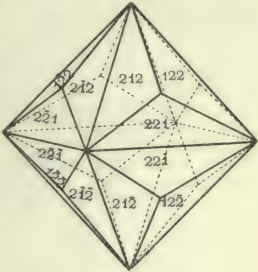


FIG. 99.  
The Triakis Octahedron {221}.

(7) The last holohedral form of the cubic system, the **tetrakis hexahedron**, is produced when one of the indices is zero, that is, when each face is parallel to one of the crystallographic axes, and when the other two indices are unlike (if alike the dodecahedron is the solid produced). Its poles all lie on the 3 great circles formed by the intersection of the three axial planes with the sphere, that is, on the primitive circle and the two axial diameters. Its {210} representative is shown in Fig. 100. It may be regarded as a cube the faces of which have been replaced by a low four-faced pyramid, or as produced by the disappearance of the medium edges of the hexakis octahedron, the two faces on each side of each such medium edge having coalesced into one. Each face is an isosceles triangle, the 12 longer sides (one in each triangle) being identical with the edges of the cube, and the 24 shorter ones meeting in fours on the crystallographic axes. The goniometrical angle over the longer edges, that is, the angle between the normals to each pair of faces intersecting in a longer edge, in the cases of the two tetrakis hexahedra most frequently met with, has the following values :

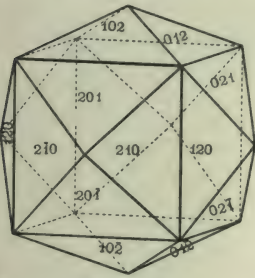


FIG. 100.  
The Tetrakis Hexahedron {210}.

The goniometrical angle over the longer edges, that is, the angle between the normals to each pair of faces intersecting in a longer edge, in the cases of the two tetrakis hexahedra most frequently met with, has the following values :

For {210}, 36° 52'; for {310}, 53° 8'.

The angle over the shorter edges is the same in the case of the form {210} as it is over the longer edges, namely, 36° 52', but in the case of {310} it is different, namely, 25° 51'.

There are also eight six-faced solid angles the apices of which lie on the four trigonal axes, the quoins being composed of three longer and three shorter edges, alternately arranged.

The simplest form, {210}, that represented in Fig. 100, is exhibited by fluor-spar,  $\text{CaF}_2$ .

Combinations of the three forms last described and the three primary forms are shown in the next three illustrations, Figs. 101, 102, and 103.

Fig. 101 represents a combination of the cube (faces marked *c*), octahedron (*o*), and rhombic dodecahedron (*d*) with the icositetrahedron  $\{211\}$ , the faces of which are marked with the letter *i*. The solid angles of the last-named predominating solid are replaced by smaller faces of the three primary forms, and the figure illustrates clearly the fact that the faces of the cube, icositetrahedron, octahedron, and rhombic dodecahedron, always follow each other in the same zone. Also the icositetrahedron  $\{211\}$  lies in the same cross-zones with the dodecahedron faces alone, so that the faces of this particular form  $\{211\}$  directly replace the dodecahedron edges. Other icositetrahedra do not thus exactly, in parallel fashion, blunt the edges of the dodecahedron, but modify either the solid angles terminating on the crystallographic axes or those occupying the middle of the octants. Fig. 102 represents a rhombic dodecahedron (*d*) the three-edged solid angles of which are all modified by small faces, marked *t*, of the triakis octahedron  $\{221\}$ . Fig. 103 represents the combination of the octahedron (*o*) and

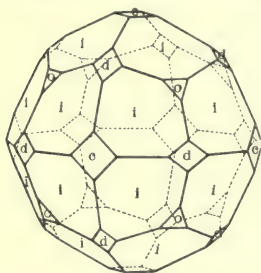


FIG. 101.

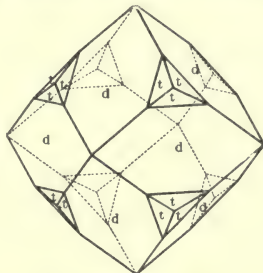


FIG. 102.

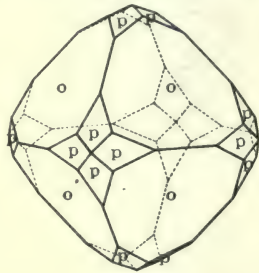


FIG. 103.

Combinations of Holohedral Cubic Forms.

tetrakis hexahedron  $\{210\}$ , the solid angles of the preponderating octahedron being all modified by four little faces of the latter form, marked *p*.

#### *List of Forms in Class 32.*

In the following list we have a summary of the forms belonging to class 32, which have now all been fully described :

$\{100\}$ Cube or hexahedron.	$\{hko\}$ Tetrakis hexahedron.
$\{110\}$ Rhombic dodecahedron.	$\{hkk\}$ Icositetrahedron.
$\{111\}$ Octahedron.	$\{hhl\}$ Triakis octahedron.
	$\{hkl\}$ Hexakis octahedron.

All the substances mentioned in the foregoing discussion of cubic forms, namely, rock salt, fluor-spar, galena, spinel, magnetite, garnet, diamond, and leucite, belong to this class 32 of perfect cubic symmetry. Rock salt, sodium chloride,  $\text{NaCl}$ , was formerly, on the evidence of pentagonal icositetrahedral etch-figures now recognised to have been immature (longer action of the solvent producing hexakis-octahedral figures), supposed to belong to the pentagonal icositetrahedral class 29, like potassium and ammonium chlorides,  $\text{KCl}$  and  $\text{NH}_4\text{Cl}$ ; it is now, however, regarded as truly holohedral of class 32. A very interesting photomicrograph showing very perfect cubes of rock salt is reproduced in Fig. 104 on Plate II. It shows a field in a crystal of quartz under only a low power (one-inch objective with small stop, and a low power eyepiece). Three large cavities are revealed, the two larger of which each contain a saturated aqueous solution of sodium chloride, a cube of the salt which has crystallised out, and a bubble of water-vapour. The smaller of these two cavities has the further remarkable attribute of taking the shape of a quartz crystal, a hexagonal



FIG. 104. — Cavities in a Quartz Crystal containing saturated Solution and Cubic Crystals of Sodium Chloride.

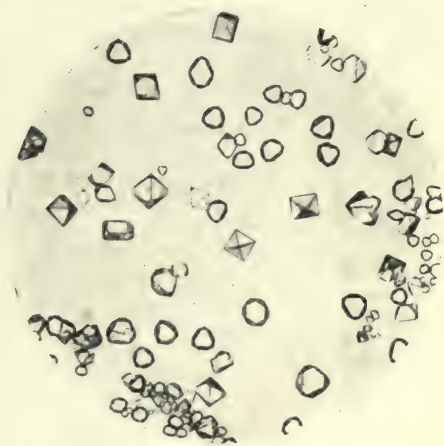


FIG. 121. — Octahedral Crystals of Caesium Alum growing from aqueous Solution.

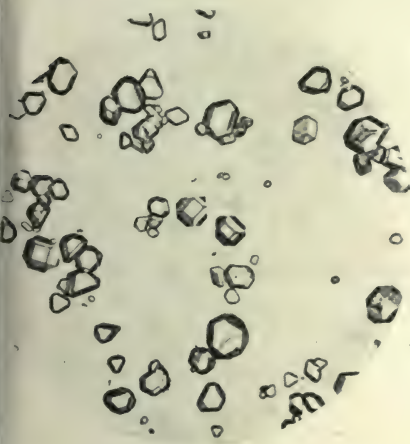


FIG. 122. — Crystals of Potash Alum growing from aqueous Solution.

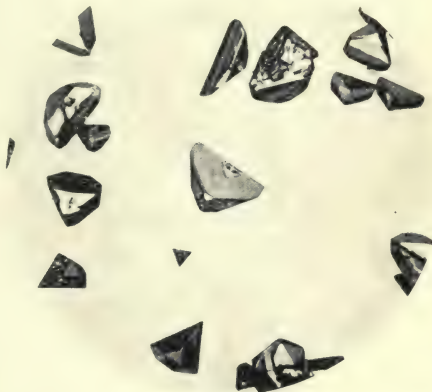


FIG. 131. — Tetrahedral Crystals of Sodium Sulphantimoniate growing from aqueous Solution.

REPRODUCTIONS OF PHOTOMICROGRAPHS OF CUBIC CRYSTALS SLOWLY GROWN FROM SOLUTION.





prism terminated by the two complementary rhombohedra; it is, as it were, a negative crystal, like the water-flowers (Fig. 442, p. 546) produced by heat rays passing through ice.

The diamond has been usually classed as hexakis tetrahedral, in class 31, but it will be shown in Chapter XXVIII. (see Fig. 397) that it is really holohedral, of class 32. The largest diamond yet found was the "Cullinan," discovered in the Premier mine near Pretoria, South Africa, in the year 1905. It weighed 3025·7 English carats or 621·2 grams (1·37 lb. avoirdupois), an English carat being then 205·3 milligrams, and was 4 inches in its largest dimension. It was presented to King Edward VII. in 1907, and when cut furnished two brilliants of 516·5 and 309·2 carats, each larger than any other cut diamond, besides 7 other large brilliants and nearly a hundred smaller brilliants. The celebrated Koh-i-noor, for instance, presented to Queen Victoria by the East India Company in 1850 and which was in Queen Mary's crown, weighed 186 carats when first cut in India, but was reduced by re-cutting in this country to 106 carats.

The "carat," the standard of weight used for precious stones, until the year 1914 was 205·3 milligrams as employed in the United Kingdom, as above mentioned, 151·4 carats being contained in one troy ounce. By an Order in Council of October 16, 1913, the British carat was legally fixed at the round metric figure of 200 milligrams, the change being ordained to occur on April 1, 1914. This was the outcome of a recommendation of the International Committee of Weights and Measures in 1905 and of the Metric Convention of 1907, and by 1912 the weight of 200 milligrams was in use in fifteen countries, including France and Germany. In that year the National Association of Goldsmiths also recommended its adoption in this country, and the Board of Trade then proceeded to arrange for the Order in Council.

The origin of "carat" is probably connected with *Ceratonia siliqua*, the carob or locust tree so common on the shores of the Mediterranean Sea, the seeds of which are very uniform in size so as to be useful as small rough weights; their pod, the "locust bean" or "St. John's bread," is horn-shaped, and its name is derived from the Greek word for horn, *κεράτιον*. Both the Greek carat and the Roman *siliqua* were used for weighing gold as well as precious stones and pearls, and as 24 of either were contained in Constantine's gold *solidus* (one-sixth of the troy ounce) it is likely that this is the origin of the method of denoting the fineness of gold. Thus the 22 carat gold of the British coinage contains 22 parts of pure gold and 2 parts of the baser metal employed to increase its durability.

The natural crystals of many "native" metals, for instance gold, platinum, silver, lead, and copper, also belong to class 32.<sup>1</sup>

**Practical Goniometrical Considerations regarding Holohedral Cubic Crystals.**—There are three methods of recognising the various forms which are developed on a cubic crystal. We have first the appearance, and it is of immense help in deciphering a complicated crystal showing numerous forms to be able, owing to familiarity with them, to recognise the seven holohedral types now discussed at sight. This would be fairly easy if the various faces were relatively equally developed, as they have been drawn in the illustrations now given. They are represented thus, with a convenient point taken as centre and all the faces drawn in equipoise and equidistant from that centre, in order to exhibit the ideal symmetrical figure in which the planes of symmetry may be at once apparent. They are all drawn to scale, with the axes arranged according to the convention to be explained in Chapter XXV., according

<sup>1</sup> For the structure as revealed by X-rays of rock salt, potassium chloride, diamond, fluor-spar, spinel, and magnetite, and of native copper, silver, gold, and lead, see Chapter XXXIII.

to which parallel faces appear as such, in order to avoid the uncertainty which would be introduced as to whether certain faces were intended to be parallel or not, if they were drawn in ordinary perspective. Such ideal crystals are, however, but very rarely seen in actual practice, and in this book it is the author's special purpose to smooth the way to practical work. As the faces, therefore, cannot be expected to be found in exact equipoise, a very mature judgment and familiarity is required to detect the faces of the various forms, and even then, in the end, except perhaps as regards such simple forms as the cube, octahedron, and dodecahedron, or occasionally the icositetrahedron (which in garnet, for instance, is often characteristically clearly displayed, as shown in Fig. 132), the second and third methods have to be employed before the crystallographer can be certain as to the forms present.

The second method of recognition of forms is by means of the angles, which, as already stated, are fixed, definite, and invariable for all cubic forms. This is, of course, the only trustworthy test. The angles of all the seven forms, as regards the two commonest representatives in each case where more than one representative is possible, have been given in the present chapter, to simplify the identification. It will be observed that all these angles are fixed by the nature of the symmetry itself, the cubic being the only system in which this is the case.

The third method, that by the position of the pole of any face on the stereographic projection, is bound up with the second method, and the construction of the stereographic projection should be the first act after a few preliminary goniometrical measurements. In the presence of numerous forms, it becomes difficult to recognise the angles of the various specific forms, owing to intermediate faces of other forms intervening; and several angles require to be added together, in order to obtain the form angle. But when the poles are carefully plotted out on the stereographic projection, it becomes easy to recognise the various forms, both by the actual positions of the poles on the projection and by the angles between them, obtained, if necessary, by adding together the intermediate angles which make them up, as just indicated.

In Fig. 105 is given the stereographic projection of a combination of all the seven holohedral forms of the cubic system. It appears complicated, but as the four quadrants are symmetrically alike, it is only necessary to study one quadrant. The seven forms are indicated both by their indices and by significant letters, poles marked *c* belonging to cube faces, those marked *o* to the octahedron, *d* stands for the rhombic dodecahedron, *h* for the hexakis octahedron {321}, *i* for the icositetrahedron {211}, *t* for the triakis octahedron {221}, and *p* for the tetrakis hexahedron {210}. The letter *p* is used to designate the last-mentioned form because *t* is already adopted for the triakis octahedron, and because the two hemihedral forms of the tetrakis hexahedron are the pentagonal dodecahedra to be described under class 30. The poles of the faces of these several forms can, therefore, be readily identified.

In the next chapter two actual examples of cubic crystals, a garnet and a crystal of cobaltite, showing several of these forms, will be



goniometrically worked through, their stereographic projections constructed step by step from the measurements, and the determination of the indices of the more complex forms described, together with the mode of carrying out all necessary calculations.

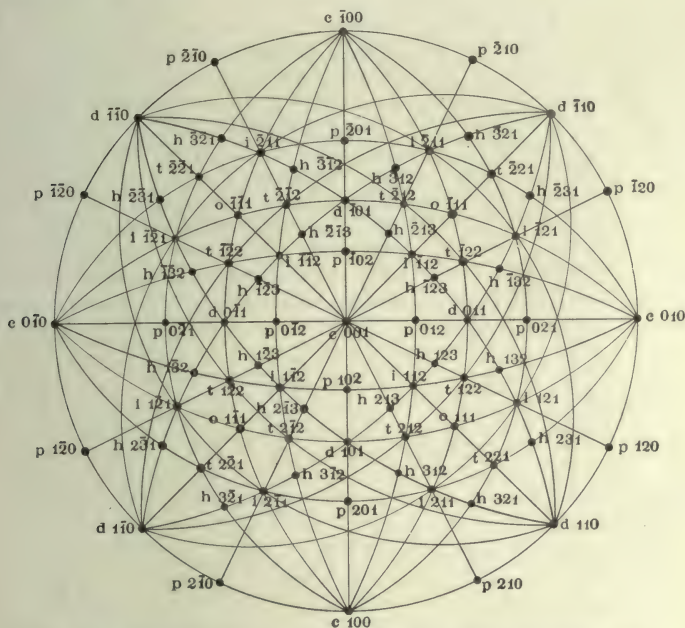


FIG. 105.—Stereographic Projection of the seven Holohedral Cubic Forms.

THE SO-CALLED HEMIHEDRAL AND TETARTOHEDRAL FORMS OF THE CUBIC SYSTEM.

*Class 31.—Hexakis Tetrahedral Class, also called Tetrahedrite Class. Hemihedrism of the Inclined-Face Character. Type, Ditesseral Polar.*

In the crystals of this class the three axial planes are no longer symmetry planes, but the other six diagonal planes of symmetry remain. The effect is to cause the digonal axes also to disappear, and to convert the 3 tetragonal axes into digonal axes of ordinary or simple symmetry, although it will be seen that they still remain tetragonal axes of compound or reflective symmetry. The stereographic projection of the symmetry axes and of the general form ( $hkl$ ) is given in Fig. 106, which is Fig. 82 repeated here for convenience.

The general form in question, called the **hexakis tetrahedron**, is shown in Fig. 107, which represents the form {321}. It was formerly considered as the hemihedral form of the hexakis octahedron, derived by suppression of the faces in alternate octants. But it is more conformable to the theory of crystals as homogeneous structures to regard it as the solid figure obtained by the repetition of any face ( $hkl$ ), having 3

different index numbers, about the particular elements of symmetry distinguishing this class. There are really two such solids, a positive and a negative, corresponding to the two possibilities of choice of alternate octants, but the two are seen to be identical when turned about and examined separately, provided the 3 index numbers are the same. No face on this solid has a parallel face. The diamond is occasionally found in hexakis tetrahedra. The left one of the two top diamonds in the set of ten shown in Fig. 820 in Chapter LI. is clearly of hexakis tetrahedral habit, as is also the diamond shown at *b* in Fig. 397 in Chapter XXVIII.

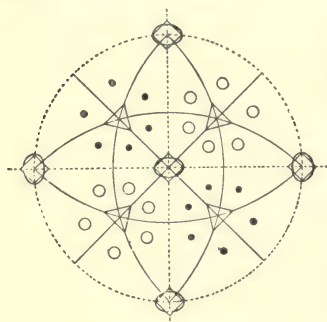


FIG. 106.—Class 31.

and brought over intact from the medium edges the angle is  $59^{\circ} 5'$ .

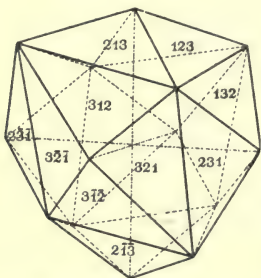


FIG. 107.—The Hexakis Tetrahedron.

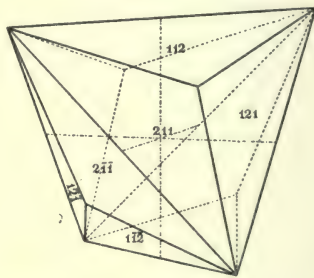


FIG. 108.—The Triakis Tetrahedron.

If we next consider what happens to the icositetrahedron, in which we have two equal indices which are less than the third, the common form being  $\{211\}$ , we find that it becomes the **triakis tetrahedron**, or trigonal dodecahedron, shown in Fig. 108.

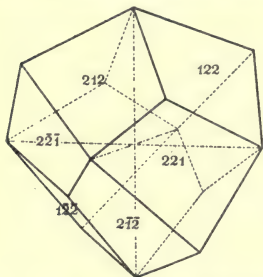


FIG. 109.—The Deltoid Dodecahedron.

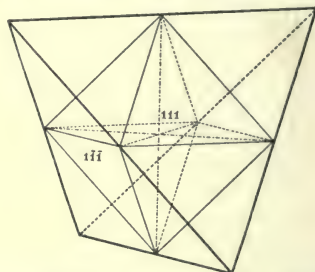


FIG. 110.—Relation of Tetrahedron to Octahedron.

The two varieties, positive and negative, are found to be identical when examined irrespective of their positions *in situ*. The longer edges are those of the regular tetrahedron, and the angle over these edges, between the normals to the pairs of faces forming them, in the case of  $\{211\}$  is  $70^{\circ} 32'$ , the angle of the octahedron. The

three faces forming a low pyramid on each tetrahedron face, and meeting in the three shorter edges, have the same inclination over these edges as they have on the original icositetrahedron.

The holohedral triakis octahedron, with two equal indices greater than the third, for instance the common form  $\{221\}$ , becomes the **deltoid dodecahedron**, shown in Fig. 109, under the operation of the symmetry elements of this class. The faces of this solid, as its name implies, are deltoidal four-sided figures, with two pairs of equal sides, the angles of the figure being such that one diagonal joins opposite equal angles and the other unequal ones. The two complementary forms appear identical when regarded away from their positions of derivation. In the case of  $\{221\}$  the angles over the new hemihedral edges are right angles, the other interfacial angles over the edges of the three-faced pyramids remaining as in the triakis octahedron.

The octahedron under the operation of class 31 symmetry becomes the regular **tetrahedron**, Fig. 111, the manner of origin being illustrated in Fig. 110, in which the tetrahedron is drawn in thick lines and the original octahedron in thin lines. The two varieties, the positive and negative tetrahedra, are only distinguishable by their different position when *in situ* as derived. The tetrahedron has six equal edges over

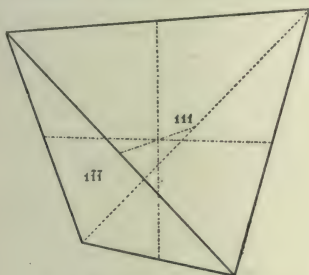


FIG. 111.—The Tetrahedron.

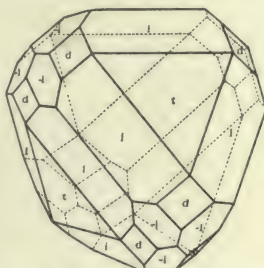


FIG. 112.—Fahl-ore, Tetrahedrite.

which the angle is  $109^\circ 28'$ , between the normals to the two faces intersecting in the edge. Each face of the tetrahedron is an equilateral triangle.

The tetrahedron is so characteristic a form of grey copper ore, fahl-ore,  $\text{Cu}_3\text{SbS}_3$ , that this mineral is commonly called tetrahedrite, and the name "tetrahedrite class" is often given to the type of symmetry of class 31. Fig. 112 represents a crystal of tetrahedrite, exhibiting the faces of the positive tetrahedron  $t = \{111\}$ , the rhombic dodecahedron  $d = \{110\}$ , and the positive and negative triakis tetrahedra  $i = \{211\}$  and  $-i = \{2\bar{1}1\}$ . The composition is essentially  $\text{Cu}_3\text{SbS}_3$ , but the copper is often partially replaced by small quantities of iron, silver, zinc, or mercury.

To summarise, we have the following forms in this class :

#### List of Forms in Class 31.

$\{100\}$ Cube or hexahedron.	$\{hko\}$ Tetrakis hexahedron.
$\{110\}$ Rhombic dodecahedron.	$\{hkk\}$ Positive triakis tetrahedron ; $\{h\bar{k}k\}$ negative triakis tetrahedron.
$\{111\}$ Positive tetrahedron ; $\{1\bar{1}1\}$ negative tetrahedron.	$\{hhl\}$ Positive deltoid dodecahedron ; $\{h\bar{h}l\}$ negative deltoid dodecahedron.
	$\{hkl\}$ Positive hexakis tetrahedron ; $\{h\bar{k}l\}$ negative hexakis tetrahedron.

**The Real Nature of Hemihedrism and Tetartohedrism.**—The cube, the rhombic dodecahedron, and the tetrakis hexahedron still retain their



full number of faces under the operation of class 31 symmetry. A similar fact will be shown to hold as regards the two former with respect to all the other three classes of the cubic system also.

This fact raises a very interesting question. In discussing the elements of symmetry in Chapter IX. it may have been remarked that, while emphasising axes and planes of symmetry as the true elements of symmetry, no mention was made of what has formerly been considered a natural division of crystals into **holohedral**, possessing all the faces of a form, **hemihedral**, in which half the faces of a form are suppressed, and **tetartohedral**, in which a form is represented by only a quarter of the holohedral number of faces. The reason is that our recently acquired full knowledge of the geometry of homogeneous structures (to be dealt with in Chapter XXX.) has led us to recognise that it is not merely a freak or whim of nature which is occurring, causing the suppression of a half or a quarter of the possible faces of a form, but that it is the definite operation of a distinct and lower combination of elements of symmetry which is occurring; and that this is owing to the specific stereometric arrangement of the atoms in the molecules of the substance of which the crystal is composed (and to the mutual arrangement of the individual molecules in the group in the cases of polymolecular crystal-units), which only permits them to arrange themselves in accordance with this particular class of symmetry, which latter is high enough to bring the crystal into the system in question, but not into the highest class of that system.

It is evident that this is a much more scientific and trustworthy explanation of the so-called hemihedral and tetartohedral forms, and there is every probability that in it we have now arrived at the true meaning of hemihedrism and tetartohedrism. These two terms may now, therefore, disappear, except as being of historic interest. The term "holohedral," however, may be retained, as it affords a concise expression for the maximum symmetry possible to any system.

An exceptionally interesting prophetic statement was made by Professor Story Maskelyne in his *Morphology of Crystals*, in which, some years before the completion of the work on homogeneous structures, he says with remarkable prescience: "The whole treatment of crystallographic symmetry on the assumption of planes and axes of symmetry, actual or potential, represents a geometrical abstraction, that needs for its development and due explanation a complete science of position applied to the molecular mass-centres, competent to embrace not merely the relative distribution *inter se*—the *intermolecular* distribution—of the chemical molecules constituting the crystallised substance, but also the *intramolecular* arrangement of the atoms whereof the molecules of the substance are themselves composed. Then the true significance of the ideal planes and axes of symmetry will be understood; and they will assuredly retain a place in the explanation of crystalline symmetry, since they rise into recognition directly from the fundamental principle of rationality of indices and are controlled by its consequences."

The literal fulfilment of this prediction has now come to pass, and axes and planes of symmetry are no longer mere geometrical abstrac-

tions but the proved elements of crystal symmetry, based on the solid groundwork of incontrovertible knowledge concerning the homogeneous partitioning of space, and the possible modes of packing therein, of the chemical molecules or polymolecular groups (crystal-units) in space-lattices and of the atoms of which they are composed in regular point-systems.

The fact that the cube and rhombic dodecahedron are present on a crystal, the other forms of which are those of class 31 (or as we shall also see, of class 30, 29, or 28), does not mean, therefore, that we are to regard these forms on the crystal as holohedral, and therefore as belonging to class 32, and only the others as belonging to class 31. The cube and rhombic dodecahedron (as well as also the tetrakis hexahedron in the case of the class 31 now under discussion) being permitted to have all their faces developed under the strict symmetry conditions exclusively dominating class 31, it is certain that the **whole** crystal, on which the development of these two forms is observed alongside the forms indubitably belonging to class 31, has been developed under the operation of the elements of symmetry solely governing class 31; for it is unthinkable that adjacent precisely similar molecules of one and the same definite chemical substance, under like conditions of temperature, pressure, and environment, can be deposited according to two different types of homogeneous structure belonging to different crystal classes. It is the very essence of the geometrical theory of crystal structure based on homogeneous partitioning, unquestionably supported from the practical experimental standpoint by the results of the author's investigations of the alkali sulphates, selenates, and double salts, that, given these identical conditions, a substance of definite chemical composition is characterised by an equally definite crystalline form. Polymorphism, the only other alternative, only enters into the range of possibility when those conditions are different.

It is, therefore, certain that the cube and rhombic dodecahedron on such crystals as we are discussing are present as forms of class 31, and not as forms of the holohedral class 32. It may also occur, moreover, and indeed very often does occur, that the two kinds of hexakis tetrahedron, triakis tetrahedron, deltoid dodecahedron, or simple tetrahedron, are both simultaneously developed on a crystal, and to such approximately equal extents that at first sight the holohedral forms from which they are derived appear to be present, combined in all probability with cube or rhombic dodecahedron faces or both, to render the verisimilitude still more complete. But the deception is as a rule only momentary, for close inspection such as accompanies goniometrical investigation usually at once reveals the fact that the faces of the positive and negative complementary forms differ in their power of reflecting light, due to their different physical character, one of the complementary forms being composed of dull faces and the other of brilliant ones. Moreover, the two kinds of faces frequently bear striations or other markings, which are characteristically different in the two cases. Hence, the physical character of the faces affords an

excellent criterion of their grouping into positive and negative complementary forms of separate individuality, or of their combined nature as a complete holohedral form. For instance, in the case of the two complementary triakis tetrahedra  $i=\{211\}$  and  $-i=\{2\bar{1}\bar{1}\}$  of tetrahedrite, shown on the crystal represented in Fig. 112, the faces of the former are striated perpendicularly to the dodecahedron edge which it truncates, while those of the latter are striated parallel to the dodecahedral edge.

Further, the faces of the cube and rhombic dodecahedron on crystals of the classes of lower symmetry than class 32 also frequently bear striations of a definitely distinctive character.

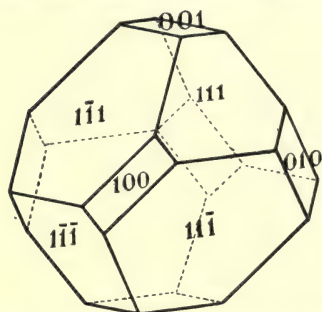


FIG. 113.—A Crystal of Zinc Blende.

For instance, the mineral zinc blende, sulphide of zinc,  $\text{ZnS}$ ,<sup>1</sup> belongs to the class 31 under discussion, and although it usually exhibits clearly tetrahedral forms—as in the case illustrated in Fig. 113 (a combination of the two primary tetrahedra  $\{111\}$  and  $\{1\bar{1}\bar{1}\}$ , developed to different extents, with small faces of the cube  $\{100\}$ )—it is sometimes found in cubes the faces of which, however, exhibit diagonally arranged striations, due to rapidly recurring attempts at producing a tetrahedron,

always succeeded by persistent and more extensive growth of the cube. On the other hand, iron pyrites,  $\text{FeS}_2$ , belongs to the next class to be considered, class 30, and is frequently also found in cubes; but these are striated parallel to alternate pairs of the edges, that is, to one of the crystallographic axes in each case, in accordance with the symmetry of that class, in which the three axial planes are planes of symmetry, and so that the striations on each face are at right angles to those on the adjacent faces. (See Fig. 120 in description of class 30.) Thus these markings on the faces of the cubes of the two substances indicate that they belong to different classes of the cubic system, and classes which are other than the holohedral class 32.

If natural markings be absent, treatment of the faces by a very minute quantity of a solvent for the crystallised substance will generally produce "etched figures," of different complementary or (if no planes of symmetry be developed) oppositely enantiomorphous shape, on the faces of the two positive and negative forms of the lesser symmetry, and also figures on the faces of the cube and rhombic dodecahedron which are not identical with those produced on a truly holohedral crystal, and which indicate more or less clearly the class of symmetry to which the crystal belongs.

*Class 30.—Dyakis Dodecahedral Class, also called Pyrites Class. Parallel-faced Hemihedrism. Type, Tesseral Central.*

The crystals of this class retain the 3 equal diagonal axes and 4

<sup>1</sup> For the structure of zinc blende as revealed by X-rays see Chapter XXXIII.



equal trigonal axes of class 31, but the 6 diagonal planes of symmetry disappear and instead the crystal is symmetrical about the 3 axial planes, the faces of the cube.

The general form  $\{hkl\}$ , in accordance with this symmetry, the form which may be regarded as derived from the hexakis octahedron, is the **dyakis dodecahedron**, which gives its name to the class. The  $\{321\}$  representative is shown in Fig. 115, and the

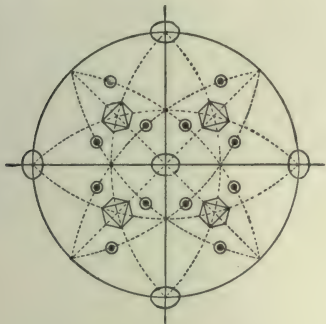


FIG. 114.—Class 30.

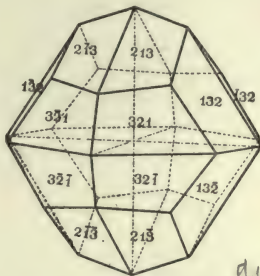


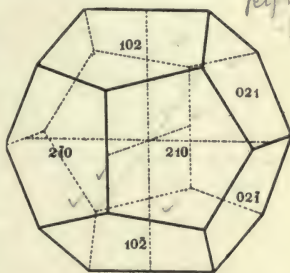
FIG. 115.—The Dyakis Dodecahedron.

stereographic projection, on which the axes of symmetry of the class are also shown, is given in Fig. 114, which is Fig. 81 repeated here for convenience of reference.

The dyakis dodecahedron consists of 12 parallel pairs of trapezoidal faces, and the four edges bounding each face are of three kinds, that is, two are equal and the other two are unequal and different from the equal pair. The longest and the shortest lie in two of the 3 symmetry planes, and the pair of equal intermediate edges meet a third intermediate edge, in which two adjacent faces intersect, to form an equiangular 3-faced solid angle in the middle of each octant, the points lying on the trigonal axes, which latter are also in this class hexagonal axes of compound symmetry. The positive and negative forms only differ so long as they are *in situ*, that is, as regards their positions; a quarter of a revolution of either brings it into the position of the other, when it cannot be distinguished from it. In the case of  $\{321\}$  the angle over any longest edge is  $30^\circ 0'$ , over any shortest edge  $64^\circ 37'$ , and over the intermediate edges  $38^\circ 13'$ .

The cube, octahedron, rhombic dodecahedron icositetrahedron, and triakis octahedron retain their full number of faces under the operation of the symmetry of this class, so that unless they bear superficial markings such as striations these forms cannot be distinguished from class 32 forms, produced under the operation of the full symmetry of the cubic system.

The form  $\{hkl\}$ , however, which is the tetrakis hexahedron in the case of the fully symmetrical class 32, becomes under the action of the lower symmetry of class 30 the **pentagonal dodecahedron**, shown in Fig. 116, which represents the positive or left one having the indices  $\{210\}$  of the two possible varieties which together correspond to the tetrakis hexahedron  $\{210\}$ , and which are only different when *in situ* as derived. The faces of this solid are pentagons with four equal sides and a fifth side of different length, which is considerably longer in the case

FIG. 116.  
The Pentagonal Dodecahedron.

of  $\{210\}$ , and which is parallel to one of the crystallographic axes. For  $\{210\}$  the angles over these longer edges are  $53^\circ 8'$ , and over the shorter edges  $66^\circ 25'$ .

The regular (pentagonal) dodecahedron of geometry,<sup>1</sup> shown in Fig. 117, possessing faces with five equal edges and angles, is not a possible crystal form, as the indices  $h$  and  $k$  in  $\{h k 0\}$  for this polyhedron are irrational. The actual values are  $\frac{h}{k} = \frac{1 + \sqrt{5}}{2}$ , a ratio involving a surd and obviously irrational. Hence, this particular case of the pentagonal dodecahedron is crystallographically inadmissible.

In a similar manner the regular icosahedron, shown in Fig. 118, is never exhibited by crystals, as its faces, which are equilateral triangles and are twenty in number, cannot be expressed by symbols with rational indices. The  $m$  corresponding to Weiss's symbol  $a : ma : ma$  for the icositetrahedron, or the Millerian  $\frac{h}{k}$ , which have the values 2 and 3 respectively for the two common icositetrahedra  $\{211\}$  and  $\{311\}$ , instead of being a whole rational number in the case of the regular icosahedron have the value 2.4142 or  $\tan 67^\circ 30'$ .

The pentagonal dodecahedron  $\{210\}$  is so particularly characteristic of iron pyrites,

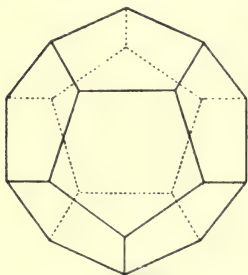


FIG. 117.—The Regular Dodecahedron.

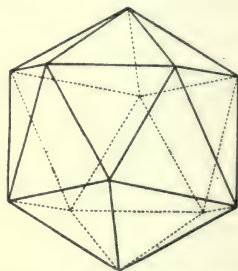


FIG. 118.—The Regular Icosahedron.

$\text{FeS}_2$ , that not only is it often called the pyritohedron, but also the whole of class 30 is frequently termed the pyrites class. Fig. 119 represents a typical crystal of pyrites as obtained from the island of Elba, which exhibits the pentagonal dodecahedron  $\{210\}$  in combination with the cube and octahedron.

This common variety of the pentagonal dodecahedron of pyrites exhibits positive thermo-electric properties, a current flowing from the copper wire with which contact is being made with the crystal and connection thereby established to a delicate galvanometer, to the crystal when the latter is gently warmed. Now it is exceedingly interesting that this variety of the pentagonal dodecahedron is striated parallel to the cube edges, as is indicated by the linear shading on Fig. 119. Moreover, when pyrites is found in simple cubes, they are always striated, the striations upon any face being at right angles to those on the adjacent faces, as shown in Fig. 120. These striations are likewise due to repeated attempts to form the pentagonal dodecahedron

<sup>1</sup> It will be remembered that there are five and only five regular convex polyhedra (Euclid xiii., the concluding deduction), namely, the cube, the octahedron, the tetrahedron, the regular icosahedron, and the regular dodecahedron. The first three are the well-known crystal forms of the cubic system shown in Figs. 84, 85, and 111, and fully dealt with on pages 144, 145, and 159. The regular icosahedron, Fig. 118, has twenty faces, all equilateral triangles, five of which meet at each of the twelve vertices. The regular dodecahedron, Fig. 117, has twelve faces each of which is a regular pentagon, and twenty vertices at each of which three of the pentagonal faces meet. In accordance with Euler's theorem, the number of edges on any of these regular polyhedral solids is less by two than the sum of the numbers of faces and vertices. The regular dodecahedron and icosahedron have each, therefore, thirty edges.

{210}, attempts which only succeed to a relatively slight extent, the cube resuming its growth almost immediately, and thus forming the vastly predominating partner in the oscillatory combination. On the other hand the much rarer variety of pentagonal dodecahedron of pyrites {120} which exhibits negative thermo-electric properties, the current passing from the crystal to the copper wire during the experiment just referred to, shows striations in the directions perpendicular to those of the first variety of positive nature, that is, at right angles to the singular edge, which is also the longest in {120} as it is in {210}, of the pentagon and parallel to the line of symmetry of the pentagonal face. While, as just explained, the oscillatory alternation of the cube and pentagonal dodecahedron {210} is responsible for the common positive striations, a rapid alternation of the pentagonal dodecahedron {120} with the dyakis dodecahedron {412} or with the icositetrahedron {211} produces the rarer negative striations. Indeed the dyakis dodecahedron and the icositetrahedron generally actually predominate in the cases of negatively thermo-electrical pyrites crystals, while the cube and pentagonal dodecahedron predominate on positive crystals. [See also Chapter LIX.]

In this very striking manner are the left (positive) {210} and right (negative) {120}

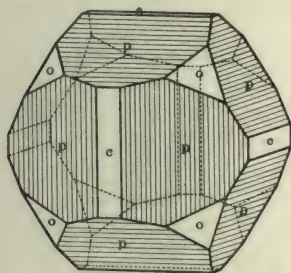


FIG. 119.—Iron Pyrites, Striated Pyritohedron with Cube and Octahedron.

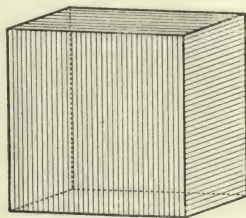


FIG. 120.—Striated Cube of Pyrites.

varieties of the pentagonal dodecahedron distinguished in the typical case of pyrites,<sup>1</sup> thus affording most important confirmatory evidence of the separate nature of the two forms.

The dyakis dodecahedron and the pentagonal dodecahedron are the only two new forms introduced by the operation of class 30 symmetry.

In brief, we have the following forms to distinguish in this class :

*List of Forms in Class 30.*

{100} Cube or hexahedron.	{hkk} Icositetrahedron.
{110} Rhombic dodecahedron.	{hhl} Triakis octahedron.
{111} Octahedron.	{hkl} Positive or left dyakis dodecahedron ;
{hk0} Positive or left pentagonal dodecahedron ; {kh0} negative or right pentagonal dodecahedron.	{khl} negative or right dyakis dodecahedron.

One of the most important and beautifully crystallising series of isomorphous salts, the alums, belongs to this class 30 of the cubic

<sup>1</sup> For the structure of pyrites, and of its isomorph hauerite  $\text{MnS}_2$ , as revealed by X-rays, see Chapter XXXIII.



system. They are double sulphates and selenates of the composition  $R'M'''\left(\begin{smallmatrix} S \\ Se \end{smallmatrix} O_4\right)_2 \cdot 12H_2O$ , where R may be sodium Na, potassium K, rubidium Rb, caesium Cs, thallium Tl, ammonium  $NH_4$ , or a substituted ammonium (in which H is replaced by an organic radicle); and M may be aluminium Al, ferric iron Fe, chromium Cr, titanium Ti, vanadium V, gallium Ga, rhodium Rh, indium In, or iridium Ir. Caesium aluminium alum,  $CsAl(SO_4)_2 \cdot 12H_2O$ , is particularly interesting as forming large clear crystals on which the octahedron and pentagonal dodecahedron {210} are present in about equal development. Under the microscope, small crystals of caesium alum, growing from a drop of only slightly supersaturated (metastable) solution placed in a shallow covered cell (formed by a hardened gold-size ring on the microscope slip), show mainly the octahedron, as very clearly exhibited by the reproduction of a photomicrograph in Fig. 121 on Plate II. (facing page 154). The two common alums (potash and ammonium alums),  $KAl(SO_4)_2 \cdot 12H_2O$  and  $NH_4Al(SO_4)_2 \cdot 12H_2O$ , usually crystallise in octahedra slightly modified by subsidiary cube and rhombic dodecahedron faces. A photomicrograph of potash alum showing these three forms is reproduced in Fig. 122, also on Plate II. But from a solution containing hydrochloric acid crystals are deposited which exhibit also good faces of the pentagonal dodecahedron {210}.

*Class 29.—Pentagonal Icositetrahedral Class, also called Cuprite Class.*

*Hemihedrism, Plagihedral or Gyrohedral. Type, Tesseral Holoaxial.*

This class is distinguished by possessing all the axes of symmetry of the cubic system but none of the planes of symmetry.

There is only one new solid introduced, however, and this is the **pentagonal icositetrahedron** which gives its name to the class, and which is the class 29 repre-

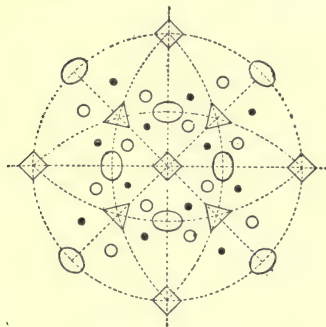


FIG. 123.—Class 29.

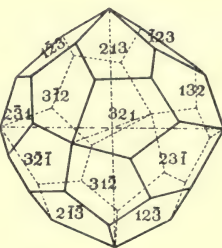


FIG. 124.



FIG. 125.

Left and Right Pentagonal Icositetrahedra.

sentative of the fully symmetric class 32 hexakis octahedron. The cube, octahedron, rhombic dodecahedron, icositetrahedron, triakis octahedron, and tetrakis hexahedron are all represented by their full number of faces under the action of class 29 symmetry. Hence, they cannot be distinguished from the fully symmetric class 32 forms unless they possess facial markings or actually show the pentagonal icositetrahedron developed. As this is a very rare occurrence, undoubted examples of the class are

equally rare. Cuprite has been shown by Sir Henry Miers to be one of these few cases. The pentagonal icositetrahedron is enantiomorphous, and as such the two possible varieties are distinct forms of the solid, which cannot be brought into identity by rotation. They behave as mirror-images of each other, or as a right-hand glove does to a left-hand one. The two varieties, corresponding together to the {321} hexakis octahedron, are shown in Figs. 124 and 125. In the previous illustration, Fig. 123, representing the symmetry elements, the repeated Fig. 80, the stereographic projection of one of them is given, that which contains the face ( $hkl$ ), in this case (321), and which is usually termed the positive or left variety, together with the projection of the symmetry axes. The projection of the other variety, right or negative, would be obtained by replacing all the dots by rings and *vice versa*, thus changing the hemisphere of every facial pole represented on the projection. Each of the 24 faces of the pentagonal icositetrahedron is a five-sided figure, no two sides being of equal length.

To summarise, we have the following forms in this class :

*List of Forms in Class 29.*

- |                |                       |                |   |
|----------------|-----------------------|----------------|---|
| {100}          | Cube or hexahedron.   | { <i>hhl</i> } | Triakis octahedron.                               |
| {110}          | Rhombic dodecahedron. | { <i>hkl</i> } | Left pentagonal icositetrahedron ;                |
| {111}          | Octahedron.           |                | { <i>khl</i> } right pentagonal icositetrahedron. |
| { <i>hk0</i> } | Tetrakis hexahedron.  |                |   |
| { <i>hkk</i> } | Icositetrahedron.     |                |   |

In Fig. 126 a crystal of cuprite<sup>1</sup> from Cornwall measured by Miers is represented, on which the faces of the pentagonal icositetrahedron {896}<sup>\*</sup> are developed, in combination with faces of the cube and octahedron. By the kindness of Sir Henry Miers the author is enabled to reproduce his drawing. Ammonium chloride,  $\text{NH}_4\text{Cl}$ , has also been shown by Slavik to be occasionally deposited from solution in well-developed pentagonal icositetrahedra of the form {943}, which exhibit cleavage parallel to the cube faces. On crystals of sylvine,  $\text{KCl}$ , from Kalusz both right and left pentagonal icositetrahedra have been observed by S. Kreutz (*Zeitschr. für Kryst.*, 1912, 51, 209), the former predominating.

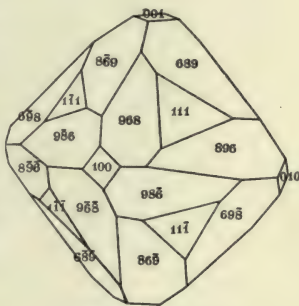


FIG. 126.—Cuprite.

*Class 28.—Tetrahedral Pentagonal Dodecahedral Class, also called Ullmannite Class. Tetartohedral Class. Type, Tesseral Polar.*

This class of crystals possesses the minimum elements of symmetry which it is possible for a crystal belonging to the cubic system to exhibit, as was clearly explained in the introduction to this chapter. The three equal and mutually rectangular crystallographic axes are no longer tetragonal axes of symmetry, but merely digonal ones; the four

<sup>1</sup> For the structure of cuprite as revealed by X-rays see Chapter XXXIII. The evidence of the X-ray analysis would appear to be more in favour of a holohedral class 32 symmetry for cuprite, rather than that of class 29.

trigonal axes of symmetry are retained but become polar, while the six digonal ones disappear altogether. There are no planes of symmetry.

The symmetry elements are clearly shown in the stereographic projection given in Fig. 127, the repeated Fig. 79, which also shows the disposition of the poles of the most general form  $\{hkl\}$  of the class. It is termed the **tetrahedral pentagonal dodecahedron**, hence the name of the class. This solid occurs in no less than four modifications, of which, however, only two are truly enantiomorphously distinct, the other two being brought by rotation to resemble these first two exactly, when moved out of their positions of derivation from the general holohedral form  $\{hkl\}$ , the hexakis octahedron. The two distinct forms are shown in Figs. 128 and 129. The first of these two figures corresponds to the form given in the stereographic projection, and is known as the left positive tetrahedral pentagonal dodecahedron. The second illustration represents the right positive tetrahedral pentagonal dodecahedron. The two forms are the mirror-images of each other, by reflection across a hypothetical rhombic dodecahedron face, which is equivalent in the stereographic projection to rotation about one of the diagonal diameters bisecting the crystallographic

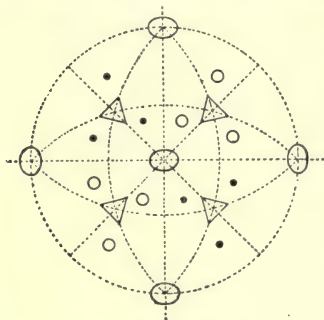


FIG. 127.—Class 28.

axial diameters. The negative right tetrahedral pentagonal dodecahedron is obtained by reflection of the left positive form shown in the projection across a cube face, or rotation about one of the crystallographic axial diameters. It is the one which is produced if the poles indicated in the projection by dots are changed into rings, and the rings into dots. Similarly, from the right positive a left negative form is obtained by reflection across a cube face. The right and left varieties of the same sign are the enantiomorphous forms, but the two right forms or the two left forms only differ in their position when *in situ*, and may be brought by rotation for  $90^\circ$  about a crystallographic axis into indistinguishable identity. The faces of both solids are unsymmetrical pentagons, in which they differ characteristically from the ordinary pentagonal dodecahedron.

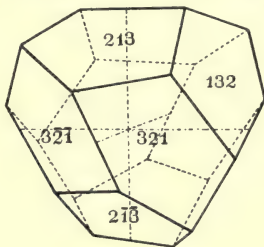


FIG. 128.

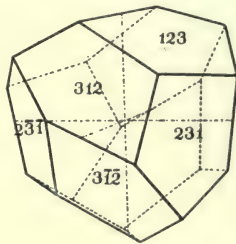


FIG. 129.

Left and Right Positive Tetrahedral Pentagonal Dodecahedra.

axial diameters. The negative right tetrahedral pentagonal dodecahedron is obtained by reflection of the left positive form shown in the projection across a cube face, or rotation about one of the crystallographic axial diameters. It is the one which is produced if the poles indicated in the projection by dots are changed into rings, and the rings into dots. Similarly, from the right positive a left negative form is obtained by reflection across a cube face. The right and left varieties of the same sign are the enantiomorphous forms, but the two right forms or the two left forms only differ in their position when *in situ*, and may be brought by rotation for  $90^\circ$  about a crystallographic axis into indistinguishable identity. The faces of both solids are unsymmetrical pentagons, in which they differ characteristically from the ordinary pentagonal dodecahedron.

The cube and rhombic dodecahedron are represented by their full number of faces even under the operation of these minimum elements of cubic symmetry.

The octahedron is represented by the tetrahedron, the positive and negative varieties only differing in position while *in situ*.

The icositetrahedron,  $\{hkk\}$ , where  $h$  is greater than  $k$ , yields the two triakis



tetrahedra, positive and negative. The triakis octahedron,  $\{hhl\}$ , where  $h$  is also greater than  $l$ , affords the positive and negative deltoid dodecahedra. Lastly, the tetrakis hexahedron  $\{hk0\}$  affords the left and right pentagonal dodecahedra.

Thus the only novelty in this class is the tetrahedral pentagonal dodecahedron, the four modifications of which have been described, and which may be considered as together making up, when *in situ*, the holohedral class 32 hexakis octahedron. We have, therefore, the following forms to record as belonging to class 28:

*List of Forms in Class 28.*

- $\{100\}$  Cube.
- $\{110\}$  Rhombic dodecahedron.
- $\{111\}$  Positive tetrahedron;  $\{1\bar{1}1\}$  negative tetrahedron.
- $\{hk0\}$  Left pentagonal dodecahedron;  $\{kh0\}$  right pentagonal dodecahedron.
- $\{hkk\}$  Positive triakis tetrahedron;  $\{h\bar{k}k\}$  negative triakis tetrahedron.
- $\{hhl\}$  Positive deltoid dodecahedron;  $\{h\bar{h}l\}$  negative deltoid dodecahedron.
- $\{hkl\}$  Left positive tetrahedral pentagonal dodecahedron;  $\{khl\}$  right positive tetrahedral pentagonal dodecahedron;  $\{h\bar{k}l\}$  right negative tetrahedral pentagonal dodecahedron;  $\{k\bar{h}l\}$  left negative tetrahedral pentagonal dodecahedron.

Among minerals, ullmannite,  $\text{NiSbS}$ , crystallises according to the symmetry of this class. Among chemically prepared substances, barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ , sodium chlorate,  $\text{NaClO}_3$ , and Schlippe's salt, sodium sulphantimoniate,  $\text{Na}_3\text{SbS}_3 \cdot 9\text{H}_2\text{O}$ , are noteworthy examples. Fig. 130 shows a crystal of barium nitrate measured by Wulff, which consists of a combination of the cube with a left positive tetrahedral pentagonal dodecahedron  $\{421\}$  and the two tetrahedra  $\{111\}$  and  $\{1\bar{1}1\}$ . Fig. 131 on Plate II. (facing page 154) is the reproduction of a photomicrograph of Schlippe's salt, taken while the crystals were still very slowly growing, from a drop of a slightly supersaturated (metastable) solution, placed within the shallow cell formed on the microscope glass-slip by a hardened ring of gold-size and covered (after the crystallisation had started) with a thin cover-glass. It shows a very clear development of the tetrahedron, the crystals generally consisting of the two complementary tetrahedra, one of which is developed so very much more than the other that the faces of the latter only appear as minute replacements at the corners of the predominating tetrahedron.

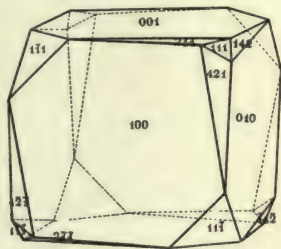


FIG. 130.—Barium Nitrate.

## CHAPTER XI

### TWO PRACTICAL EXAMPLES OF CUBIC CRYSTALS, GARNET AND COBALTITE

#### (1) Garnet. *Class 32, Cubic Holohedral.*

THE important garnet group of minerals has the general chemical composition  $R''_3R'''_2(\text{SiO}_4)_3$ , being silicates in which  $R''$  may be calcium, magnesium, iron, or manganese, and  $R'''$  may be aluminium, iron, or chromium, isomorphously replacing each other. Indeed not only may different garnets have different  $R''$  and  $R'''$  metals as their dominating elements, but one and the same garnet usually contains two or more metals of each  $R''$  or  $R'''$  group more or less, "vicariously" as it is termed, replacing each other. The general crystallographic form is the rhombic dodecahedron, but the icositetrahedron is almost as frequently and as largely developed, so that it is also characteristic of the garnet group.

The particular garnet chosen for the purpose of these typical cubic measurements is a small one, 3 to 4 millimetres in diameter, very dark red in colour, and almost an ideally perfect icositetrahedron in shape, the faces of this form being nearly equally developed. (See Fig. 98, which also gives the indices of all the front faces of the form  $\{211\}$ .) Smaller faces, apparently of the rhombic dodecahedron, and subsequently to be shown to be so in fact, may be observed truncating the twelve solid angles which are formed in each case by two longer and two shorter icositetrahedral edges. Its appearance is shown in Fig. 132 and its stereographic projection in Fig. 133.

The former figure was drawn to scale after the completion of the measurements, by the general conventional method which will be fully described in Chapter XXV., the actual construction being represented in Fig. 340. The mode of constructing the stereographic projection, as far as the rhombic dodecahedron is concerned, was fully gone into on page 148 of Chapter X., and the additional construction necessary for the insertion of the icositetrahedral poles and the zone-circles including them will be described during the course of the measurements.

The shape of the crystal being so obviously that of the icositetrahedron, and the small truncations being so clearly situated at the apparently correct positions for faces of the rhombic dodecahedron,





such as  $(1\bar{1}0):(211)$  terminating at the  $d$ -poles on the primitive circle.

(5) It was also advisable to obtain confirmatory measurements across the 6 main quoins or solid angles of the icositetrahedron, that is, to measure the angle between either pair of opposite  $i$ -faces of each quoin. These angles should be  $70^\circ 32'$  (the same as the octahedral angle) if the icositetrahedron present be  $\{211\}$ ; and the zones containing them, two such angles in each, will also each contain a pair of dodecahedral faces at  $54^\circ 44'$  from each of the adjacent  $i$ -faces of the zone (the half-supplement of the octahedral angle). The two secondary diameters at  $45^\circ$  to the edges of the page indicate 2 of the 6 zones in question, and the other 4 are indicated by the arc-zones such as  $(101):(121)$  terminating at the ends of the principal diameters. The measurement of this fifth class of zone will finally confirm that the  $d$ -faces and the  $i$ -faces are mutually arranged as they should be if the forms are truly those of the rhombic dodecahedron  $\{110\}$  and the icositetrahedron  $\{211\}$ .

Commencing now the measurements on the lines thus planned out, by measuring the angles between the four small apparently dodecahedral faces of one of the zones referred to under (1), we set the crystal up on the wax holder of the goniometer by one of the 6 axial quoins, so as to bring one of the cubic crystallographic axes vertical, just as the crystal stands in Fig. 132, and with the four little  $d$ -faces to be measured approximately parallel to the axis of the goniometer and parallel in pairs to the two adjusting movements. Adjusting now these faces accurately with the aid of the tangent screws, and finally centring the crystal, we proceed to the actual measurement. The following readings were obtained for the three such zones on the crystal, treated precisely similarly in this manner, the crystal being reset for the second and again for the third so as to bring the second and third crystallographic axes in turn vertical and parallel to the goniometer axis.

### 3 PRINCIPAL DODECAHEDRAL ZONES.

Circle Reading.	Angle.	Circle Reading.	Angle.	Circle Reading.	Angle.
$\left\{ \begin{array}{l} d \ 360^\circ \ 0'A \\ d \ 269 \ 59 \\ d \ 179 \ 59 \ A \\ d \ 90 \ 0 \ A \\ d \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} dd \ 90^\circ \ 1' \\ dd \ 90 \ 0 \\ dd \ 89 \ 59 \ A \\ dd \ 90 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} d \ 271^\circ \ 12' \\ d \ 181 \ 13 \\ d \ 91 \ 21 \\ d \ 1 \ 14 \\ d \ 271 \ 12 \end{array} \right.$	$\left\{ \begin{array}{l} dd \ 89^\circ \ 59' \\ dd \ 89 \ 52 \\ dd \ 90 \ 7 \\ dd \ 90 \ 2 \end{array} \right.$	$\left\{ \begin{array}{l} d \ 340^\circ \ 15'A \\ d \ 250 \ 14 \ A \\ d \ 160 \ 15 \ A \\ d \ 70 \ 14 \\ d \ 340 \ 15 \end{array} \right.$	$\left\{ \begin{array}{l} dd \ 90^\circ \ 1'A \\ dd \ 89 \ 59 \ A \\ dd \ 90 \ 1 \\ dd \ 89 \ 59 \end{array} \right.$

It will be clear from these angular values that the faces are indeed either those of the rhombic dodecahedron or of the cube (assuming cubic symmetry), or of a tetragonal or rectangular rhombic prism, the angles being all so close to  $90^\circ$  that there can be no doubt of nature's intention to make them precisely  $90^\circ 0'$ . That they are really faces of the rhombic dodecahedron and not of the cube or other rectangular form is rendered probable by the fact that the four faces of the three zones were all different ones, there being 12 faces altogether. The values obtained in the first and third of the zones never differ by more than a minute from  $90^\circ$ , and the two middle values of the second zone only show more difference because the faces affording them were of poorer

quality, some slight malformation resulting in blurred images of the Websky signal. In a case like this we must judge the symmetry absolutely by the individual values, those marked "A" by preference, as being fully trustworthy; for to take the mean would be to obtain 90° 0' anyhow, a result perfectly worthless as regards any indication of the symmetry, although after having decided the latter we may take the mean as representing the final measured value of the angle.

We may next pass on to the measurement of a zone of type (2), consisting of both *d*- and *i*-faces, say that containing the right *d*-face shown in Fig. 132 along the equatorial edges of the crystal (the face (110)), the *i*-face which forms the right upper one of the central four shown in the figure (the face (211)), and the adjoining upper *d*-face along the middle crystal edges of the vertical plane (the face (101)). Setting the crystal so that this zone was approximately adjusted parallel to the goniometer axis, and then completing the final adjustment with the aid of the tangent screws, the following measurements were obtained. Alongside are also given those for a second similar zone, that corresponding to the other diagonal diameter of the projection.

DIAGONAL DODECAHEDRAL ZONES.

Circle Reading.	Angle.		Circle Reading.	Angle.	
<i>d</i> 360° 0'A	<i>di</i> 30° 0'	<i>dd</i> 60° 0'A	<i>d</i> 360° 0'A	<i>di</i> 30° 5'	<i>dd</i> 60° 0'A
<i>i</i> 330 0	<i>id</i> 30 0		<i>i</i> 329 55	<i>id</i> 29 55	
<i>d</i> 300 0 A	<i>di</i> 30 3		<i>d</i> 300 0 A	<i>di</i> 30 2	
<i>i</i> 269 57	<i>id</i> 29 54	<i>dd</i> 59 57	<i>i</i> 269 58	<i>id</i> 29 55	<i>dd</i> 59 57
<i>d</i> 240 3	<i>di</i> 30 6		<i>d</i> 240 3	<i>di</i> 30 1	<i>dd</i> 60 7
<i>i</i> 209 57	<i>id</i> 29 55	<i>dd</i> 60 1	<i>i</i> 210 2	<i>id</i> 30 6	
<i>d</i> 180 2 A	<i>di</i> 30 0		<i>d</i> 179 56	<i>di</i> 30 0	
<i>i</i> 150 2	<i>id</i> 30 6	<i>dd</i> 60 6	<i>i</i> 149 56	<i>id</i> 29 56	<i>dd</i> 59 56
<i>d</i> 119 56	<i>di</i> 29 56		<i>d</i> 120 0	<i>di</i> 29 58	
<i>i</i> 90 0	<i>id</i> 29 58	<i>dd</i> 59 54	<i>i</i> 90 2	<i>id</i> 29 58	<i>dd</i> 59 56
<i>d</i> 60 2	<i>di</i> 30 4		<i>d</i> 60 4	<i>di</i> 30 4	<i>dd</i> 60 2
<i>i</i> 29 58	<i>id</i> 29 58	<i>dd</i> 60 2	<i>i</i> 30 0	<i>id</i> 29 58	
<i>d</i> 0 0 A			<i>d</i> 0 2 A		

The two other similar zones were also measured, but the angular values obtained were so close to those above given that it is unnecessary to set them forth at length here, the two quoted being ample for the purpose of determining the symmetry and deciding as to whether the angles are truly 60° and 30°. An inspection of the lists at once shows that there can be no doubt on the point, the greatest discrepancy being only 7', and in the two cases where absolutely irreproachable "A" images of the signal were concerned, the values were precisely 60° 0'. We can consequently definitely decide that nature intended the angles to be truly *dd*=60° 0', and *di*=30° 0', that the conditions of (2) for the forms {110} and {211} are absolutely fulfilled, and that the *d*-faces of the three rectangular zones first measured are truly those of the rhombic dodecahedron. Having thus decided the question of the symmetry, **and not before**, we may be permitted to record the mean of the values as the final measured value in the case of each of the two angles *dd* and *di*.

It may be here remarked that the faces of the icositetrahedron were

slightly striated, parallel to the axis of the zone now in question, that is, parallel to the edges of intersection with the two adjacent dodecahedron faces belonging to the same zone. The images were therefore occasionally slightly affected by this circumstance, hence the small deviations of a few minutes from exactly  $30^{\circ} 0'$  in the angles. The effect of these striations will be shown to disappear entirely when we come to measure the zones perpendicular to them, across the quoins, under (5), so that absolutely no doubt is introduced by the fact of the slight striation.

We next tackle the question of the value of the icositetrahedral angles across the longer edges, referred to under (3).

Setting the crystal almost upright on the wax as in Fig. 132, but just tilted over slightly so as to bring one of the longer edges, say that which passes upwards from the central quoin in the figure, parallel to the goniometer axis, and then adjusting the two faces on each side of and forming the edge, with the aid of the tangent screws, we find that on rotating the crystal on the goniometer the zone comprises only these two and the parallel pair of icositetrahedral faces. It is unnecessary to measure all 12 such zones; four of them, judiciously selected, say two involving one quoin and two involving another of the 6 quoins in a complementary manner, will be fully adequate to afford us definite information as to the symmetry. Four such were measured, and the values in the cases of a pair of them are recorded below.

LONGER-ICOSITETRAHEDRAL-EDGE ZONES.

Circle Reading.	Angle.	Circle Reading.	Angle.
$\left\{ \begin{array}{l} i \ 360^{\circ} \ 0' \\ i \ 311 \ 51 \\ i \ 180 \ 4 \\ i \ 131 \ 51 \\ i \ 0 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} ii \ 48^{\circ} \ 9' \\ ii \ 131 \ 47 \\ ii \ 48 \ 13 \\ ii \ 131 \ 51 \end{array} \right.$	$\left\{ \begin{array}{l} i \ 360^{\circ} \ 0' \\ i \ 311 \ 53 \\ i \ 180 \ 0 \\ i \ 131 \ 45 \\ i \ 0 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} ii \ 48^{\circ} \ 7' \\ ii \ 131 \ 53 \\ ii \ 48 \ 15 \\ ii \ 131 \ 45 \end{array} \right.$

None of the images were of "A" quality owing to the slight striation, which was sufficient in these zones to blur the images somewhat; but the latter were quite certain to within two or three minutes, so that the values of *ii* may be taken as trustworthy within those approximate limits. It will be seen at once that the value of the angle over the longer edges is very close indeed to  $48^{\circ} 11'$ , the theoretical angle for {211}, and as a matter of fact the mean of all the values obtained is exactly  $48^{\circ} 11'$ . For the values in the other pair of similar zones measured were very close to those recorded above and the mean afforded was identical. The measurements of these longer-edge zones, therefore, fully establish the identity of the icositetrahedron as {211}.

Passing on now to the measurement of the shorter-edge zones, as indicated under (4) to be advisable, a very slight further tilting of the crystal will enable one of them to be set conveniently on the wax, and with the aid of the tangent screws the adjustment to the axis of the goniometer of the shorter edge selected is only a matter of a moment or two. The measurement of four of these zones will also suffice, and the actual readings for two of them are next recorded. Instead of only containing the adjusted pair of icositetrahedral faces and the parallel pair, however, each of these zones is found to contain also a parallel pair of the little dodecahedral faces, each



symmetrically placed in the centre of the obtuse angle between the icositetrahedral faces.

SHORTER-ICOSITETRAHEDRAL-EDGE ZONES.

Circle Reading.	Angle.	Circle Reading.	Angle.
$d\ 360^\circ\ 0'$ $i\ 286\ 51$ $i\ 253\ 16$ $d\ 180\ 0$ $i\ 106\ 42$ $i\ 73\ 9$ $d\ 0\ 0$	$di\ 73^\circ\ 9'$ $ii\ 33\ 35$ $id\ 73\ 16$ $di\ 73\ 18$ $ii\ 33\ 33$ $id\ 73\ 9$	$i\ 360^\circ\ 0'$ $i\ 326\ 28$ $d\ 253\ 15$ $i\ 179\ 59$ $i\ 146\ 28$ $d\ 73\ 13$ $i\ 0\ 0$	$ii\ 33^\circ\ 32'$ $id\ 73\ 13$ $di\ 73\ 16$ $ii\ 33\ 31$ $id\ 73\ 15$ $di\ 73\ 13$

It will be clear that the angle *ii* across the shorter edges of the icositetrahedron corresponds to the theoretical angle  $33^\circ\ 33'$  for {211}. The four individual values of *ii* are all within 2' of this angle, and their mean is precisely  $33^\circ\ 33'$ . The values obtained from two other of these twelve zones, judiciously selected again so as to afford the maximum confirmation of the symmetry, yielded almost identical values, leaving no room for doubt that the icositetrahedron present is {211}.

We come now, finally, to the measurement of the angles across the quoins, as suggested in (5). Let us commence, say, by measuring the zone containing the upper right (211) icositetrahedral face, of the four central faces shown in Fig. 132, and the lower left face ( $2\bar{1}\bar{1}$ ). The complete zone will include also the two parallel faces at the back of the crystal as it is represented in the figure, and also the two little dodecahedral faces on the upper right and lower left margin of the figure, that is, those two at the ends of the  $45^\circ$ -diagonal which passes from the right upper to the left lower intermediate corners on the outside periphery of the figure, namely, (011) and ( $0\bar{1}\bar{1}$ ). The setting of the crystal on the wax for this zone is a very easy matter, the crystal being merely tilted so as to bring the diagonal just referred to horizontal, and one of the icositetrahedral faces can be adjusted with one tangent screw, and one of the dodecahedral faces with the other, to which it should preferably have been set preliminarily as nearly parallel as possible.

When the adjustment was completed for each of the four of these six zones which in turn were measured, it was found, as already suggested would be the case, that all effect of striation had disappeared, the striations being now horizontal and parallel to the zone plane and thus perpendicular to the signal-images, which latter were absolutely sharp. The readings obtained were consequently of great precision, affording the most absolute confirmation of the supposition that the forms present were the rhombic dodecahedron and the icositetrahedron {211}. Those for two of the zones are given below.

ICOSITETRAHEDRAL CROSS-QUOIN ZONES.

Circle Reading.	Angle.	Circle Reading.	Angle.
$d\ 360^\circ\ 3'A$ $i\ 305\ 20\ A$ $i\ 234\ 48\ A$ $d\ 180\ 3\ A$ $i\ 125\ 19\ A$ $i\ 54\ 48\ A$ $d\ 0\ 4\ A$	$di\ 54^\circ\ 43'A$ $ii\ 70\ 32\ A$ $id\ 54\ 45\ A$ $di\ 54\ 44\ A$ $ii\ 70\ 31\ A$ $id\ 54\ 44\ A$	$d\ 360^\circ\ 0'A$ $i\ 305\ 17\ A$ $i\ 234\ 45\ A$ $d\ 180\ 0\ A$ $i\ 125\ 18\ A$ $i\ 54\ 45\ A$ $d\ 0\ 0\ A$	$di\ 54^\circ\ 43'A$ $ii\ 70\ 32\ A$ $id\ 54\ 45\ A$ $di\ 54\ 42\ A$ $ii\ 70\ 33\ A$ $id\ 54\ 45\ A$

The separate values of the angle  $ii$  across the quoin (between opposite  $i$ -faces) are thus seen to be within a single minute of the theoretical angle for the icositetrahedron  $\{211\}$ , namely  $70^\circ 32'$ , and the angles  $di$  and  $id$  indicating the position of the two dodecahedron faces with respect to the faces of  $\{211\}$  are also all within  $2'$  of the theoretical equal angles of  $54^\circ 44'$ , assuming the little faces to be truly those of the rhombic dodecahedron. The values for the other two zones of this type measured gave also the same within  $2'$ .

We have now very thoroughly explored this crystal of garnet, and it only remains to present the main results in tabular form, provided we accept as well known the theoretical values of the angles of the icositetrahedron  $\{211\}$ , as recorded in the last chapter. But there is no occasion to assume them at all, for they are quite easily calculated from first principles, and as it will be an excellent exercise so to calculate them, we shall proceed to do so, before presenting the table of results in which the measured angles are comparatively recorded alongside the theoretical ones. In the cubic system there are no elements to calculate, for the axial angles  $\alpha$ ,  $\beta$ , and  $\gamma$  are all  $90^\circ$ , and the lengths of the axes are all equal, and may be regarded as unity. Moreover, no basal angle or angles are necessary for the calculation of the angles of cubic crystals, however complicated, for the perfect symmetry of the system provides that the angles of the simplest of the primary forms, the rhombic dodecahedron, are  $90^\circ$  and  $60^\circ$ , and the angles between the faces of this form and those of the axial-plane form, the cube, are  $45^\circ$ . These data are adequate to enable us to calculate any angle between any faces of any cubic crystal whatsoever. It has already been shown in the last chapter (page 149) how we may calculate the octahedron angle,  $70^\circ 32'$ , from these premises fixed by the nature of the symmetry. We will now proceed, therefore, on similar lines to calculate the angles between adjacent faces of the icositetrahedron  $\{211\}$ , and between those of this form and adjacent ones of the rhombic dodecahedron. The stereographic projection given in Fig. 133 shows all the necessary triangles. It was constructed in the manner already described in the last chapter for Fig. 92.

To find the angles  $di = (101) : (112)$  and  $ii = (112) : (\bar{1}\bar{1}2)$ .

We can find both from the same right-angled triangle  $C = (001) : d = (101) : i = (112)$ , for  $Ci$  is the half of  $ii$ . The right angle is at  $i$ , and if we construct the Napierian diagram for the triangle, as described for Fig. 53, on page 107, and illustrated by numerous examples in Chapter VIII., we may derive from it the following equations, by Napier's rules:

$$\begin{aligned} \sin di &= \sin 45^\circ \sin 45^\circ, & \cos 45^\circ &= \cot 45^\circ \tan Ci, \\ &= \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} & \text{or } \tan Ci &= \cos 45^\circ \tan 45^\circ; \\ &= \frac{1}{2} & &= \frac{1}{\sqrt{2}} \cdot 1 \\ di &= 30^\circ. & & \end{aligned}$$

$$Ci = 35^\circ 16'.$$

$$\text{Angle over quoin, } ii = 2Ci = 70^\circ 32'.$$

Thus the angle  $ii = (112) : (\bar{1}\bar{1}2)$  over the top quoin in Fig. 132, or the similar angle over any other of the 6 quoins, such, for instance, as the central quoin  $(211) : (2\bar{1}\bar{1})$ , is

70° 32', which is the same as the octahedron angle, a fortuitous occurrence owing to the high degree of symmetry.

The angle  $di = (110) : (112)$  of the same zone is  $= 90^\circ - 35^\circ 16' = 54^\circ 44'$ .

The angle  $di = (101) : (112)$  has been shown above to work out to 30°. Hence, the complementary angle of the zone,  $dd = (101) : (\bar{1}\bar{1}0)$ , is 60°, for  $di = (\bar{1}\bar{1}0) : (112)$  is 90°. Thus we independently prove one of the dodecahedron angles previously assumed. In fact, all the angles of cubic crystals follow from the simple assumption that the poles of the rhombic dodecahedron are at 45° from the cube poles, that is, that they bisect the cube angles of 90°.

To find the angle  $ii = (211) : (\bar{2}\bar{1}\bar{1})$ , the angle over the longer edges.

We can most conveniently find the half of the angle, namely,  $iP$ , where P is the point of intersection of the arc with the diameter AC, from the right-angled triangle  $APi$ , in which the right angle is at P, the angle at A is 45°, and the side  $Ai$  is 35° 16', being half the angle  $ii$  over the quoin at A. When the conditions are set forth in a Napierian diagram we deduce by the rules :

$$\begin{aligned}\sin \frac{1}{2}ii &= \sin 35^\circ 16' \sin 45^\circ : \\ \frac{1}{2}ii &= 24^\circ 5\frac{1}{2}' \\ \text{and } ii &= 48^\circ 11' .\end{aligned}$$

Thus the icositetrahedral angle (for  $\{211\}$ ) over the longer edges works out to be 48° 11', the theoretical angle quoted in the last chapter.

The angle over the other long edge of the initial face (211), between that face and  $(2\bar{1}\bar{1})$ , may be equally easily calculated. For the half of this angle is represented by the portion of the diameter  $Ci = (001) : (211)$  which lies between (211) and the primitive circle, which it intersects at the possible pole of (210), and we can find the arc  $(211) : (210)$  from the triangle  $i = (211) : (210) : d = (110)$ , in which we know that the angle at (210) is a right angle, the angle at  $d$  is the complement of 35° 16', and  $di$  is 30°. If we work out the Napierian equation we shall obtain as the result that  $\text{Log. } \sin (211 : 210) = \bar{1}.61091$ , which corresponds to 24° 5½', and thus affords us the same value 48° 11' for the double angle  $ii$ , the angle over the second long edge, as we have just found for the angle over the first long edge.

To find the angle  $ii = (211) : (121)$  over the shorter edges of the icositetrahedron  $\{211\}$ .

We can find the half again most conveniently,  $iX$ , from the triangle formed by these two points ( $i$  and X) and  $d = (110)$ , in which we know that the angle at X is a right angle, the arc  $id = 30^\circ$ , and the angle at  $d$  is 35° 16' (same as  $Ci = (001) : (\bar{1}\bar{1}2)$ ). From the Napierian diagram we get :

$$\begin{aligned}\sin iX &= \sin 30^\circ \sin 35^\circ 16' \\ iX &= 16^\circ 46.7' = \frac{1}{2}ii .\end{aligned}$$

Angle over short edge  $ii = 33^\circ 33'$ .

We can now finally confirm that the angles over all the 6 quoins are the same, taking the case of the angle between (121) and  $(\bar{1}\bar{2}\bar{1})$  as a second example. We can get  $\frac{1}{2}ii$  from the triangle  $BiM$ , where M is the intersection of (121) :  $(\bar{1}\bar{2}\bar{1})$  with the diameter CB. In this triangle the angle at M is a right angle, that at B is 45°, and  $iM$  is half the angle over the long edge, namely 24° 5½'.

If we construct a Napierian diagram we can deduce thence the equation :

$$\sin iB = \frac{\sin 24^\circ 5\frac{1}{2}'}{\sin 45^\circ} ,$$

and working this out by logarithms as usual we find that  $\text{Log. } \sin iB = \bar{1}.76142$ , which corresponds to  $iB = 35^\circ 16'$ , and  $2(iB) = ii =$  the angle over the quoin  $(121) : (\bar{1}\bar{2}\bar{1}) = 70^\circ 32'$ . This is identical with the other quoin-angle  $2Ci$  already found in the first calculation, so that we have now fairly established the value of the quoin-angle by taking two independent examples, and without any assumption that the equality can be proved purely geometrically.



This completes the calculations of angles. A word or two remain to be said as to the symbols of the icositetrahedron faces. The angles both measured and calculated have settled definitely the positions of the faces and their poles, but it has yet to be proved that the indices of the form are  $\{211\}$ . This, however, can immediately be done by cross-multiplication of the zone-symbols of a pair of zones to which the icositetrahedral face under consideration is common; for each such face lies on two of the primary arc-zones shown both in the projection, Fig. 133 and in Fig. 92 in the last chapter, that is, those arc-zones in which occur the poles of the cube and rhombic dodecahedron.

The initial pole of the icositetrahedron, the face corresponding to which gives its symbol to the form, namely (211), is situated at the intersection of the zone  $[(100) : (011)]$  with the zone  $[(110) : (101)]$ . We first find the symbol of each of these zones by cross-multiplication of the symbols of the two faces determining it, and then cross-multiply the zone-symbols in order to arrive at the symbol of the face the pole of which lies at their intersection, as described in Chapter VI.

$$\begin{array}{rcl}
 1 & 0 & 0 & 1 & 0 & 0 \\
 & \times & \times & \times & & \\
 0 & 1 & 1 & 0 & 1 & 1 \\
 & & & & & \\
 1 & 1 & 0 & 1 & 1 & 0 \\
 & \times & \times & \times & & \\
 1 & 0 & 1 & 1 & 0 & 1 \\
 & & & & & \\
 0 & \bar{1} & 1 & 0 & \bar{1} & 1 \\
 & \times & \times & \times & & \\
 1 & \bar{1} & \bar{1} & 1 & \bar{1} & \bar{1}
 \end{array}
 \begin{array}{l}
 = [0\bar{1}1] \\
 \\
 = [1\bar{1}\bar{1}] \\
 \\
 = (211)
 \end{array}$$

Thus the symbol of the face occupying this position at the intersection of the two zones, one a cube-dodecahedral zone and the other a dodecahedral zone, is in fact (211).

We may similarly verify the indices of the two other faces in the first octant (121) and (112), by cross-multiplication of the zone-symbols of the zones at the intersections of which they lie. This is done below:

The first of these faces is common to the two zones  $[(110) : (011)]$  and  $[(010) : (101)]$ .

$$\begin{array}{rcl}
 1 & 1 & 0 & 1 & 1 & 0 \\
 & \times & \times & \times & & \\
 0 & 1 & 1 & 0 & 1 & 1 \\
 & & & & & \\
 0 & 1 & 0 & 0 & 1 & 0 \\
 & \times & \times & \times & & \\
 1 & 0 & 1 & 1 & 0 & 1 \\
 & & & & & \\
 1 & \bar{1} & 1 & 1 & \bar{1} & 1 \\
 & \times & \times & \times & & \\
 1 & 0 & \bar{1} & 1 & 0 & \bar{1}
 \end{array}
 \begin{array}{l}
 = [1\bar{1}1] \\
 \\
 = [10\bar{1}] \\
 \\
 = (121)
 \end{array}$$

The second face is common to the pair of zones  $[(011) : (101)]$  and  $[(001) : (110)]$ .

$$\begin{array}{rcl}
 0 & 1 & 1 & 0 & 1 & 1 \\
 & \times & \times & \times & & \\
 1 & 0 & 1 & 1 & 0 & 1 \\
 & & & & & \\
 0 & 0 & 1 & 0 & 0 & 1 \\
 & \times & \times & \times & & \\
 1 & 1 & 0 & 1 & 1 & 0 \\
 & & & & & \\
 1 & 1 & \bar{1} & 1 & 1 & \bar{1} \\
 & \times & \times & \times & & \\
 \bar{1} & 1 & 0 & \bar{1} & 1 & 0
 \end{array}
 \begin{array}{l}
 = [11\bar{1}] \\
 \\
 = [\bar{1}10] \\
 \\
 = (112)
 \end{array}$$

The indices of the two faces are thus seen to be those assumed, namely (121) and (112).

As regards the stereographic projection, as given in Fig. 133, it is like that of Fig. 92, already fully explained in the last chapter, except that eight additional arc-zones are constructed, one on each side of each of the four principal diameters, so as to terminate at the ends of each diameter at its intersection with the primitive circle. Those arc-zones which terminate at cube poles contain the angles over the

longer icositetrahedral edges, and those which end at *d*-poles on the primitive circle contain the angles over the shorter edges of the icositetrahedron.

Their construction can be accomplished directly by the compasses, by trial, so as to pass through the required poles, all of which are already fixed by the intersection of the arcs and diameters drawn in Fig. 92. Or they can be more systematically drawn by the usual geometrical method of constructing an arc to pass through three given points, the three determinative facial poles of the particular zone, finding the centre of the arc by the intersection of the two bisecting perpendiculars to the two lines connecting respectively the first and second and the second and third polar points.

Four subsidiary diameters may also be drawn, to pass through the poles of the icositetrahedron not already situated on the diagonal diameters at 45° to the edges of the page. This then completes the stereographic projection.

It now only remains to present the results for garnet in concise tabular form.

Table of Results for Garnet,  $R''_3R'''_2(SiO_4)_3$ .

**Crystal-system :** Cubic. **Class :** 32, cubic holohedral.  
**Habit :** Icositetrahedral.  
**Forms observed :** Rhombic dodecahedron  $d=\{110\}$ , and icositetrahedron  $i=\{211\}$ , the latter form largely predominating.  
**Interfacial angles :** as tabulated in the following list.

MORPHOLOGICAL ANGLES OF GARNET.

Angle.	No. of Measurements.	Limits.	Mean observed.	Calculated.	Difference.
$dd=(110):(1\bar{1}0)$ . .	12	89° 52'–90° 7'	90° 0'	90° 0'	0'
$\left\{ \begin{array}{l} dd=(110):(101) \\ \text{or } (101):(011) \end{array} \right.$ . .	24	59 54–60 6	60 0	60 0	0
$\left\{ \begin{array}{l} di=(110):(211) \\ \text{or } (101):(112) \end{array} \right.$ . .	48	29 54–30 6	30 0	30 0	0
$\left\{ \begin{array}{l} di=(110):(112) \\ \text{or } (101):(121) \end{array} \right.$ . .	16	54 42–54 45	54 44	54 44	0
$\left\{ \begin{array}{l} ii=(112):(\bar{1}\bar{1}2) \\ \text{or } (121):(\bar{1}21) \end{array} \right.$ . .	8	70 31–70 33	70 32	70 32	0
$\begin{array}{l} ii=(211):(2\bar{1}1) \\ \text{or } (121):(\bar{1}21) \end{array}$ . .	8	48 7–48 15	48 11	48 11	0
$\left\{ \begin{array}{l} di=(1\bar{1}0):(211) \\ \text{or } (110):(2\bar{1}1) \end{array} \right.$ . .	16	73 9–73 18	73 14	73 13	1
$\left\{ \begin{array}{l} ii=(211):(121) \\ \text{or } (2\bar{1}1):(\bar{1}21) \end{array} \right.$ . .	8	33 31–33 35	33 33	33 33	0

This concludes our investigation of garnet. It has been a very complete one as regards the morphology of the crystal; for being the first practical example of a cubic crystal, it was considered advisable to work it out in detail, in order to be of maximum use to those who desire to carry out a similar series of measurements on a garnet of like character, which can usually be obtained from any mineral dealer of standing.

(2) *Cobaltite. Arsenosulphide of Cobalt,  $\text{CoAsS}$ . Class 30, Pyrites Class of Cubic System.*<sup>1</sup>

Cobaltite is a mineral closely resembling pyrites in crystalline character, the pyritohedron, the pentagonal dodecahedron  $\{210\}$ , being usually a prominent form as in the case of pyrites. The cube and octahedron are frequently associated with the pyritohedron.

The crystal of cobaltite selected as our second example of a cubic

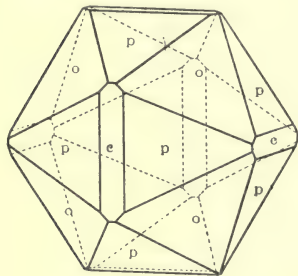


FIG. 134.

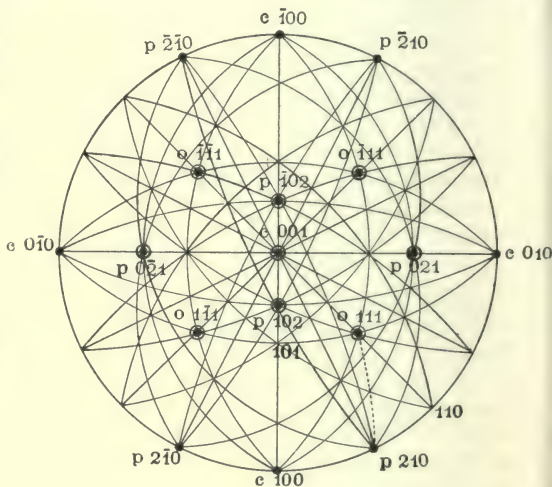


FIG. 135.

crystal was a beautiful little specimen, of a type which is readily obtained from the best mineral dealers (hence its choice as an example), roughly spherical in shape like the garnet, and of about  $3\frac{1}{2}$  millimetres diameter. It possessed a brilliant greyish-white metallic lustre, affording excellent reflections of the goniometer signal, and was altogether eminently suitable for goniometrical investigation. It is illustrated in Fig. 134, which was drawn to scale in the usual conventional manner after the completion of the measurements, the construction being described in Chapter XXV., and illustrated in Fig. 344. Its stereographic projection is given in Fig. 135, the method of constructing which will presently be described.

At first sight the crystal appears to be of a highly complicated character, consisting of a large number of triangular facets, not suggestive of any well-known cubic form. Indeed the crystal has been chosen as an example largely because of its apparent complication, and for the purpose of showing how simple it really becomes after the first few measurements have been made, clearly indicating the nature of the forms present. Careful preliminary examination with a pocket lens revealed the fact that the crystal possessed six sets of faces, each consisting of

<sup>1</sup> Sir William Bragg has brought forward some evidence from the X-ray analysis of cobaltite that the symmetry may be even a stage lower than that of pyrites, namely, that of the tetrahedral pentagonal dodecahedral class 28, in which case the octahedral faces would be those of two complementary tetrahedra. There was no evidence of this on this crystal, the eight octahedral faces being approximately equally developed and similar in character.



three faces, and of markedly similar nature, arranged about the positions of possibly cubic axes, one set at each end of each axis. Each set consisted of a central face somewhat narrow, tailing off on each long side into a triangular face, having its apex outwards, inclined to the strip-face at a relatively small angle, like a pair of pointed wings; and the edge between the strip-face and each of the two triangular faces was usually blunted by striæ, having the effect of making the two triangular faces appear as if they were joined by a curved face. The two triangular faces at the ends of the curve, however, were themselves beautifully plane and gave excellent reflections of the signal, and the central strip-face between them (separated from them by the curved parts consisting of numerous striæ) also gave "A" reflections. The circumstance of the occurrence of the striations, however, served well to identify these 6 symmetrically (cubically) placed sets of 3 faces, and it appeared not improbable that the strip-faces might actually prove to be faces of the cube, in which case the triangular faces into which they tailed at each side would be those of a pentagonal dodecahedron. The striations themselves lent additional weight to this probability, because one of the most characteristic features of the pyritohedron {210} is the striation parallel to the singular long edges (those which would be replaced by cube faces if present), as shown in Fig. 119, due to repeated alternation of attempts to produce faces of the cube and pentagonal dodecahedron, the striation being often so deep and stepped as to result in apparent curvature over the edge instead of there being a sharp edge.

The remaining triangular faces on the crystal were then seen to be eight in number, one in each octant, symmetrically placed; this would agree perfectly with the supposition that they were the faces of the octahedron. It was the fact that they were about the same size as the pyritohedron faces, and that their corners were adjacent to those of the latter at the solid angles, forming common apices, which gave the crystal the appearance of being composed of the faces of a single unknown form having triangular faces, the cube faces being mostly narrow strips only, and hence not apparent at first sight, not sensibly modifying the six edges between the pairs of triangular faces where they occurred.

Having thus from superficial observation with a pocket lens arrived at the preliminary idea that the crystal may prove to be composed of faces of three forms belonging to the cubic system, the cube, octahedron, and pentagonal dodecahedron {210}, we proceed to the measurements.

It was obvious that the six sets of possibly cube-pyritohedron faces already alluded to as being so marked, were arranged in pairs along three zones, and the proper course to take was clearly to measure these three zones first, when we should arrive at a confirmation or otherwise of our supposition as to the nature of the faces, from the magnitude of the angles found. It has already been shown in the last chapter (p. 164) that the angle over the singular long edge of the pentagonal dodecahedron {210}, which is the edge that may be modified by a cube face, is  $53^{\circ} 8'$ . If the cube face be present between the two pentagonal dodecahedral faces it will bisect this angle; that is, the angles between

the strip-like cube face and the two adjacent triangular faces of the pentagonal dodecahedron will each be  $26^{\circ} 34'$ .

We commence the measurements, therefore, by setting up the crystal on the wax by one of the cube edges, so that a zone containing two other sets of supposed pyritohedron-cube faces is adjusted for measurement, precisely, in fact, as the crystal appears in Fig. 134. It will be most convenient also to arrange the two vertical strips of cube faces (which are parallel to each other at the front and back of the crystal respectively) parallel to one of the adjusting movements, when it will be found that the other adjusting movement is parallel to two other similar strip-like cube faces which belong to this zone, horizontally arranged, however, as regards their long edges and belonging to two other sets of the faces in question, lying in a zone perpendicular to the one about to be measured, these two cube faces being common to both zones.

After the completion of the measurements for the zone thus adjusted, the crystal was reset in a position  $90^{\circ}$  from the first setting, and after the adjustment and measurement of this second similar cube zone the third of these zones was set, by another rearrangement of the crystal on the wax-holder, at a position  $90^{\circ}$  to both the first and second settings, and then also adjusted and measured. The readings obtained are set forth below. In order to distinguish clearly the various faces in a case like this it is an excellent plan to make little drawings of their shapes, showing their relative sizes, opposite the readings and label-letters, as is shown in the case of the first of the three zones recorded.

### 3 CUBE ZONES.

Shape of Face.	Circle Reading.	Angle.
	<i>c</i> $360^{\circ} 0'A$	<i>cp</i> $63^{\circ} 20'A$
	<i>p</i> $296 40 A$	<i>cc</i> $89^{\circ} 57'A$
	<i>c</i> $270 3 A$	<i>pc</i> $26 37 A$
	<i>p</i> $243 31$	<i>cp</i> $26 32$
	<i>c</i> $180 0 A$	<i>pc</i> $63 31$
	<i>p</i> $116 34$	<i>cc</i> $90 3 A$
	<i>c</i> $90 0 A$	<i>cp</i> $63 26$
	<i>p</i> $63 25 A$	<i>cc</i> $90 0 A$
	<i>c</i> $0 0 A$	<i>pc</i> $26 34$
		<i>cp</i> $26 35 A$
		<i>cc</i> $90 0 A$
		<i>pc</i> $63 25 A$

Circle Reading.	Angle.	Circle Reading.	Angle.
<i>c</i> $360^{\circ} 0'$	<i>cp</i> $26^{\circ} 37'$	<i>c</i> $360^{\circ} 0'A$	<i>cp</i> $63^{\circ} 25'$
<i>p</i> $333 23 A$	<i>pc</i> $63 30 A$	<i>p</i> $296 35$	<i>cc</i> $90^{\circ} 0'A$
<i>c</i> $269 53 A$	<i>cc</i> $90^{\circ} 7'$	<i>c</i> $270 0 A$	<i>pc</i> $26 35$
<i>p</i> $206 30$	<i>cp</i> $63 23$	<i>p</i> $243 29 A$	<i>cc</i> $90 2 A$
<i>c</i> $179 55 A$	<i>pc</i> $26 35$	<i>c</i> $179 58 A$	<i>cp</i> $63 31 A$
<i>p</i> $153 22$	<i>cc</i> $89 58 A$	<i>p</i> $116 36 A$	<i>cc</i> $90 2 A$
<i>c</i> $89 55 A$	<i>cp</i> $26 33$	<i>c</i> $90 0 A$	<i>cp</i> $63 22 A$
<i>p</i> $26 34$	<i>pc</i> $63 27$	<i>p</i> $63 27 A$	<i>cc</i> $89 58 A$
<i>c</i> $0 0$	<i>cc</i> $90 0 A$	<i>c</i> $0 0 A$	<i>pc</i> $26 36 A$
	<i>cp</i> $63 21$		<i>cc</i> $90 0 A$
	<i>pc</i> $26 34$		<i>cp</i> $26 33 A$
			<i>cc</i> $90 0 A$
			<i>pc</i> $63 27 A$

There can be no doubt from these measurements that the *c*-faces are those of the cube or other rectangular solid, the angles in all three mutually perpendicular zones being evidently intended to be  $90^\circ$ . To take the mean of all these values in the neighbourhood of  $90^\circ$  would not only be useless as regards any indication of symmetry, but positively misleading, for to divide the sum of four angles together making up  $360^\circ$  by four, is to obtain as the result in any case  $90^\circ 0'$ . We must look, therefore, to the individual values for the indication of the symmetry. In 5 cases the angles actually observed, of "A" quality, were exactly  $90^\circ 0'$ , and in the other 5 "A" cases the greatest divergence was only  $3'$ . Hence, we have excellent ground for concluding that nature intended these for cube or other rectangularly inclined faces.

As regards the position of the *p*-faces between the supposed cube faces, the means of the twelve values of the two angles *cp* are respectively  $26^\circ 34'$  and  $63^\circ 26'$ . It is obvious that the individual values of the acuter angle are all within  $3'$  of the mean value  $26^\circ 34'$ , and that we can, therefore, accept this mean angle as representing the truth. This, however, is the exact angle which has been shown to occur between the faces of the cube and of the pentagonal dodecahedron {210}. The whole angle *cc* having been accepted as  $90^\circ 0'$ , the more obtuse angle *cp* must be the difference, the complement, namely,  $63^\circ 26'$ ; the 12 individual values of the angle show a maximum divergence (in one case only) of  $6'$  from the mean. But it cannot be too strongly emphasised that no deduction concerning the symmetry can be legitimately drawn from these mean values. On the contrary, we must look for any indication of real validity to the individual values, particularly to the relative values of the angles adjacent to any specific cube face, that is, the angles given by the relative positions of the signal-images yielded by two *p*-faces, one on each side of the *c*-face in question, with respect to the image yielded by the *c*-face, which is thus common to the two angles.

The fact that we have accepted the *c*-faces as being mutually rectangularly inclined by no means proves cubic symmetry. They might equally well be the faces of a prism belonging to the tetragonal or rhombic system. In order to prove cubic symmetry we have to show that the faces inclined to the *c*-faces are equally inclined in all three rectangular zones. If the inclination were only the same along two the symmetry would probably be tetragonal, and if different along all three zones it would very likely be rhombic.

Regarding now the individual values in pairs, one on each side of a *c*-face in this manner, we do come to the conclusion that every such pair of angles is so nearly equal that we may fairly assume it to have been nature's intention to have made them all exactly so. If we take first the only case of a pair of adjacent *cp* angles having "A" values, the case in the third zone where a pair of such adjacent values are  $26^\circ 36'$  and  $26^\circ 33'$ , the difference is only  $3'$ , and the difference from the mean of the whole 12 values is only  $1'$  in the one case and  $2'$  in the other. If



we take all the 5 pairs in turn other than this sixth pair, we observe that the differences of the two angles from each other are respectively, 5', 1', 3', 2', and 4'. These variations are sufficiently small to be legitimately ascribed to slight disturbances during the formation of the crystal, and the angular values may, therefore, be taken as equal with respect to the symmetry. Having thus decided, **and not before**, we may set down the mean value in the table of angles as representing the ideal angles intended by nature.

Further, respecting the symmetry. We have found that the three mutually rectangular zones (represented by the primitive circle and the two diameters parallel to the edges of the page) exhibit similar angles, each showing four angles of  $26^{\circ} 34'$  and four of  $63^{\circ} 26'$ , together making up four right angles. The symmetry, therefore, is of cubic character. But it is not of full cubic character; for, as will be plain from the stereographic projection, while there is symmetry about the three axial planes (parallel to the faces of the cube), there is not also symmetry to the  $45^{\circ}$ -diagonal planes of symmetry (parallel to the faces of the rhombic dodecahedron). The poles of the faces of the form  $p$  are only symmetrical to the two diameters parallel to the page edges, and not also symmetrical to the diameters inclined at  $45^{\circ}$  to the edges of the page. Hence the symmetry is that of class 30, the pyrites class, and not that of class 32, the holohedral class. The form  $p$  is consequently that of the pentagonal dodecahedron  $\{210\}$  and not that of the tetrakis hexahedron having the same symbol and double the number of faces; the latter would have shown a further pair of  $p$ -poles at  $26^{\circ} 34'$  on each side of the central  $c$ -pole on the horizontal diameter of the projection, and also a further pair at  $63^{\circ} 26'$  on each side of the centre on the vertical diameter, and also four more faces in the zone represented by the primitive circle. That is, we should have had the angle  $26^{\circ} 34'$  repeated 8 times in each of the three zones measured, instead of only 4 times, if the  $p$ -form had been represented by the entire number of faces possible to full cubic symmetry, in other words, had the form been the tetrakis hexahedron.

Hence, our conclusion from the study of these three first measured zones is that the symmetry is that of class 30 of the cubic system, the pyrites class, and that the forms exhibited in these three zones are the cube and the pentagonal dodecahedron  $\{210\}$ , represented in the stereographic projection and in the drawing of the crystal by the letters  $c$  and  $p$  respectively.

We pass next to the measurement of the zones containing the cube faces and those which we surmise to be octahedron faces, marked  $o$  in the figures.

Setting the crystal on the wax-holder of the goniometer, and arranging the holder in its socket so that a cube face (one of the broader strips for choice) and an adjacent octahedron face can be adjusted parallel to the goniometer axis (setting by preference the much larger and more brilliantly reflecting octahedron face parallel to one of the adjusting movements), and then adjusting and centring these two faces, we find on rotation round the zone that the latter consists of two parallel  $c$ -faces and four  $o$ -faces,

the latter in two parallel pairs. The measurements obtained from such a zone are set forth below, together with those for two other similar zones which were also measured. There are indeed six such zones altogether, all of which were measured, but three will be ample for us to record here, in order to afford adequate evidence of the symmetry. Two of the zones are indicated by the diagonal 45°-diameters in the projection, and the four others by the arc-zones constructed about the rectangular axial diameters, one pair about each, as fully described in the last chapter in connection with the construction of the stereographic projection (Fig. 92) of the three simple cubic forms, the cube, octahedron, and rhombic dodecahedron.

6 CUBE-OCTAHEDRON ZONES.

Circle Reading.	Angle.	Circle Reading.	Angle.	Circle Reading.	Angle.
<i>c</i> 360° 0'A	<i>co</i> 54° 44'A	<i>c</i> 360° 0'A	<i>co</i> 54° 41'A	<i>c</i> 360° 0'A	<i>co</i> 54° 44'A
<i>c</i> 305 16 A	<i>oo</i> 70 32 A	<i>c</i> 305 19 A	<i>oo</i> 70 33 A	<i>c</i> 305 16 A	<i>oo</i> 70 32 A
<i>c</i> 234 44 A	<i>oc</i> 54 46 A	<i>c</i> 234 46 A	<i>oc</i> 54 44 A	<i>c</i> 234 44 A	<i>oc</i> 54 43 A
<i>c</i> 179 58 A	<i>co</i> 54 42 A	<i>c</i> 180 2 A	<i>co</i> 54 44	<i>c</i> 180 1 A	<i>co</i> 54 41 A
<i>c</i> 125 16 A	<i>oo</i> 70 31 A	<i>c</i> 125 18	<i>oo</i> 70 31	<i>c</i> 125 20 A	<i>oo</i> 70 31 A
<i>c</i> 54 45 A	<i>oc</i> 54 44 A	<i>c</i> 54 47 A	<i>oc</i> 54 47 A	<i>c</i> 54 49 A	<i>oc</i> 54 48 A
<i>c</i> 0 1 A		<i>c</i> 0 0 A		<i>c</i> 0 1 A	

These excellent readings at once assure us that we are indeed dealing with the combination of the cube and the octahedron. The values of the angle *oo* are all within one minute of the exact angle of the octahedron, 70° 32', and the cube-octahedron angle *co* is only once as much as 4' removed from the theoretical value 54° 44'. The readings for the other three zones were equally good and as fully confirmatory of this conclusion. The images of the goniometer signal afforded by the octahedron faces were particularly excellent, very brilliant, single, and clearly defined.

In the last chapter the pentagonal dodecahedron {210} was stated to exhibit an angle over the shorter edges of 66° 25'. This we should next proceed to verify on our crystal.

Suppose we start by resetting the crystal so that we can measure the angle between the face (210), which is that *p*-face to the right of the front *c*-face (vertical strip) in Fig. 134, and the *p*-face (102), which lies immediately above the front *c*-face in the figure. Adjusting these two faces parallel to the goniometer axis, and then exploring the zone by rotation of the axis, we find that the zone comprises also two other parallel faces, at the back of the crystal in the figure. Three such zones were measured, and the readings for them are recorded below ; namely, besides the zone just described, a second one containing the same *p*-face (210) and the *p*-face (102̄), which is the bottom face in the figure, and a third one containing again the initial *p*-face (210) and the *p*-face (021), which is the upper one on the right side of the figure. Two other similar zones on a different part of the crystal were also measured, but the three named, and recorded below, are ample for our purpose.

## SHORTER PENTAGONAL-DODECAHEDRAL-EDGE ZONES.

Circle Reading.	Angle.	Circle Reading.	Angle.	Circle Reading.	Angle.
$\left\{ \begin{array}{l} p \ 360^\circ \ 0' \\ p \ 246 \ 29 \\ p \ 180 \ 0 \\ p \ 66 \ 24 \ A \\ p \ 0 \ 1 \ A \end{array} \right.$	$pp \ 66^\circ \ 29'$   $pp \ 66 \ 23 \ A$	$\left\{ \begin{array}{l} p \ 360^\circ \ 0' \ A \\ p \ 246 \ 26 \ A \\ p \ 180 \ 0 \ A \\ p \ 66 \ 26 \\ p \ 0 \ 0 \end{array} \right.$	$pp \ 66^\circ \ 26' \ A$   $pp \ 66 \ 26$	$\left\{ \begin{array}{l} p \ 360^\circ \ 0' \ A \\ p \ 293 \ 41 \\ p \ 180 \ 1 \\ p \ 113 \ 33 \\ p \ 0 \ 0 \end{array} \right.$	$pp \ 66^\circ \ 19'$   $pp \ 66 \ 28$

The mean of these 6 values of the acute angle  $pp$  is  $66^\circ 25'$ , exactly the theoretical value of the angle across the shorter edges (edges other than the singular long edge which in our crystal is replaced by a strip cube face) of the pentagonal dodecahedron  $\{210\}$ . The individual values are adequately near to the mean and to each other for us to accept the mean as the angle intended by nature; no question of symmetry is involved as regards the two values from one and the same zone, as they are afforded by faces obviously intended to be parallel, and the mean value for each of the three zones is practically identical (the means being respectively  $66^\circ 26'$ ,  $66^\circ 26'$ , and  $66^\circ 24'$ ). The first two zones are the pair of arc-zones about the diameter  $p=(210):c=(001):p=(\bar{2}10)$  and very close to it; the third is one of the wider arc-zones terminating at the ends of the same diameter in the stereographic projection, and it will be shown presently that the shorter or the longer arcs  $pp$  of both these types of zone are equal, in accordance with the symmetry of class 30, and with the fact that the angles across all four shorter edges of the pentagonal dodecahedron are equal.

There is only one further type of zone that obviously invites measurement, namely, that containing the angle between adjacent  $p$ - and  $o$ -faces. Six such zones were actually measured on the crystal before us, and the readings for three of them are given below.

They contained respectively the angles  $po$  between the  $p$ -face (102) above the central cube strip in Fig. 134 and the right-hand primary  $o$ -face (111) adjoining, between the same  $p$ -face (102) and the adjacent left  $o$ -face ( $1\bar{1}1$ ), and between the right central initial  $p$ -face (210) and the right primary  $o$ -face (111) adjoining. All these zones contain this angle  $op$  twice, yielded by two pairs of parallel  $o$ - and parallel  $p$ -faces. Its value will be shown during the course of the calculations to be  $39^\circ 14'$ . The measurements for the three zones specifically mentioned were as follows:

## OCTAHEDRAL-PENTAGONAL-DODECAHEDRAL ZONES.

Circle Reading.	Angle.	Circle Reading.	Angle.	Circle Reading.	Angle.
$\left\{ \begin{array}{l} p \ 360^\circ \ 0' \ A \\ o \ 320 \ 47 \ A \\ p \ 179 \ 59 \\ o \ 140 \ 48 \ A \\ p \ 0 \ 0 \ A \end{array} \right.$	$po \ 39^\circ \ 13' \ A$   $po \ 39 \ 11$	$\left\{ \begin{array}{l} o \ 360^\circ \ 0' \ A \\ p \ 320 \ 47 \ A \\ o \ 180 \ 3 \\ p \ 140 \ 48 \\ o \ 0 \ 0 \ A \end{array} \right.$	$op \ 39^\circ \ 13' \ A$   $op \ 39 \ 15$	$\left\{ \begin{array}{l} p \ 360^\circ \ 0' \ A \\ o \ 320 \ 42 \\ p \ 179 \ 59 \\ o \ 140 \ 44 \\ p \ 0 \ 0 \ A \end{array} \right.$	$po \ 39^\circ \ 18'$   $po \ 39 \ 15$



The mean of these six values of the acute angle  $op$ , the angle between adjacent  $o$ - and  $p$ -faces, is  $39^{\circ} 14'$ , which is identical with the theoretical angle assuming the  $o$ -faces to be those of the octahedron and the  $p$ -faces to be those of the pentagonal dodecahedron  $\{210\}$ . The individual values are also adequately close to indicate clearly intended identity with the mean value.

We have now very fully measured this crystal of cobaltite, and shown that the measurements agree perfectly with the assumption that the forms present are those of the cube, octahedron, and pentagonal dodecahedron  $\{210\}$ . The theoretical values of the angles have been assumed to be known, but, as in the case of garnet, we shall now no longer take this for granted, but actually calculate those angles which have not already been calculated during our investigation of garnet, or previously in the discussion of the three primary forms of the cubic system in the last chapter. The octahedron angle  $oo = 70^{\circ} 32'$  has already been calculated (p. 149), together with its half supplement, the angle between adjacent cube and octahedron faces,  $co = 54^{\circ} 44'$ . The construction of the stereographic projection has also been fully described (p. 148) and given in Fig. 92, as far as the cube and octahedron faces are concerned. The angle  $54^{\circ} 44'$  just referred to is that between the central cube face (001) of the projection and each of the four octahedron faces surrounding it, or between the parallel  $c$ -face underneath, (00 $\bar{1}$ ), and the four octahedron faces in the lower hemisphere. All these eight  $o$ -poles lie on the diagonal  $45^{\circ}$ -diameters. It is also the angle of the arc  $co$  of each of the pair of arc-zones terminating at the ends of the axial diameters parallel to the edges of the page.

The additional construction shown in Fig. 135 for cobaltite is only of a very simple character, and can be described as we proceed with the calculations.

To calculate the position of the facial poles of the pentagonal dodecahedron  $\{210\}$ , that is, to find  $cp = (100) : (210)$ .

This can best be done by utilising the principle of the anharmonic ratio of four poles in a zone, fully explained in Chapter VI. The four poles in question are  $c = (100)$ ,  $p = (210)$ ,  $d = (110)$  which is not present but the position of which is known to be  $45^{\circ}$  from either cube face, and  $c = (010)$  which we can temporarily call  $c'$  to distinguish it from (100). Applying the principle of the anharmonic ratio, we have the equation :

$$\begin{array}{r} \begin{array}{cc} 010 & 100 \\ \times & \times \\ \sin 45^{\circ} & \sin cp \\ \sin c'p & \sin 45^{\circ} \end{array} = \frac{110}{010} \cdot \frac{210}{100} \\ \begin{array}{cc} \times & \times \\ 210 & 110 \end{array} \\ \frac{\sin cp}{\cos cp} = \frac{1}{2} \cdot \frac{1}{1} \\ \tan cp = 0.5 \\ cp = 26^{\circ} 34'. \end{array}$$

It is thus seen that the anharmonic equation gives immediately the value of the tangent of the required angle  $cp$ , which is exactly 0.5. Now 0.5000 is the value of the tangent of  $26^{\circ} 34'$ , as obtained from a table of natural tangents. This is the angle which we have already assumed as the theoretical one for  $\{210\}$ , so that the accuracy

of that assumption is now definitely proved. Double the angle,  $53^{\circ} 8'$ , is the angle over the singular long edges of the pentagonal dodecahedron  $\{210\}$ , as stated in the last chapter, these six edges being replaced by the cube faces in our crystal.

We can now place the poles of the pentagonal dodecahedron in position in the stereographic projection, beginning with those on the primitive circle, namely,  $(210)$  at  $26^{\circ} 34'$  to the right of  $(100)$ , and  $(\bar{2}\bar{1}0)$  at the same angle to the left. We draw next a couple of diameters to pass through the central pole  $(001)$  and terminate at  $(210)$  and  $(\bar{2}\bar{1}0)$ . The other terminations on the upper part of the primitive circle are the poles  $(\bar{2}\bar{1}0)$  and  $(210)$ .

The other  $p$ -poles will lie on the axial diameters parallel to the edges of the page. To find one of those on the horizontal diameter, say  $(021)$ , we mark off the angle  $26^{\circ} 34'$  from  $(010)$  along the primitive circle, either up or down (indeed it will be most useful to mark off both, and to draw diameters through the centre to them, as we shall subsequently require these diameters), and join the point so marked off to the pole of the zone, that is, to  $(100)$  if the marking had been upwards or to  $(\bar{1}00)$  if it had been downwards. Where this line cuts the horizontal diameter is the pole  $(021)$ , and also the lower pole  $(0\bar{2}\bar{1})$  represented by the ring. The poles  $(0\bar{2}\bar{1})$  and  $0\bar{2}\bar{1}$  may also be inserted at the same distance to the left of the centre as the pair just found are to the right, along the horizontal diameter.

The poles  $(102)$  and  $(10\bar{2})$ , and  $(\bar{1}02)$  and  $(\bar{1}0\bar{2})$ , lie on the vertical axial diameter, and can be found by the same process, and in fact by using the same marked-off point at  $26^{\circ} 34'$  from  $(010)$ , for we have only to join this to  $(010)$ , the proper pole of the zone on which the desired pole lies, in order to get, at the intersection of the joining line with the vertical diameter, the position of the poles  $(\bar{1}02)$  and  $(\bar{1}0\bar{2})$ , or  $(102)$  and  $(10\bar{2})$ , according as the marking off had been upwards or downwards.

We have now found the positions of all the poles of the crystal faces, and it only remains, as far as the stereographic projection is concerned, to connect them by further arcs representing the other zones measured, as actually shown in Fig. 135, either by the trial method with the compasses, or by the more systematic geometrical method of first finding the proper centre from which to construct the required arc to pass through three given poles belonging to the zone.

The indices of the pentagonal dodecahedron are proved to be  $\{210\}$  by the mode of calculating the angle  $cp$ ; for we assumed those indices in the calculation, and the result of the latter,  $26^{\circ} 34'$ , coincides absolutely with the measured angle.

There are only two further angles to calculate, owing to the perfection of cubic symmetry, namely, the angle over the shorter edges of the pentagonal dodecahedron, which we have stated in the last chapter to be  $66^{\circ} 25'$  and confirmed by measurement, and of which we may take as an example either  $(210) : (021)$  or  $(210) : (102)$ , or both, and the acute angle between adjacent octahedron and pentagonal dodecahedron faces, which we have found by measurement to be  $39^{\circ} 14'$ . We shall, therefore, proceed now to calculate these two final angles from the calculated data already acquired.

**To find  $pp = (210) : (021)$  or  $(210) : (102)$ .**

We utilise the right-angled triangle  $p = (210) : p = (021) : c = (010)$ , or the similar one having the same elements  $p = (210) : p = (102) : c = (100)$ , from the Napierian diagram for either of which we derive the equation :

$$\begin{aligned}\cos pp &= \cos 63^{\circ} 26' \cos 26^{\circ} 34' \\ pp &= 66^{\circ} 25' .\end{aligned}$$

The angle  $pp$  across the shorter edges of  $\{210\}$  is thus proved to be  $66^{\circ} 25'$ , as stated in the last chapter, and as found by measurement, a further proof that the form  $p$  is indeed  $\{210\}$ .

**To find  $op = (111) : (102)$  or  $(111) : (210)$ .**

These two angles should be identical in value if the symmetry be truly cubic. To find the first we utilise the oblique-angled triangle  $c = (100) : p = (102) : o = (111)$ , in

which we know that  $cp=63^{\circ} 26'$ ,  $co=54^{\circ} 44'$ , and the included angle at  $c=45^{\circ}$ . Employing formula (b) of Chapter VII., we have :

$$\tan \theta = \tan 54^{\circ} 44' \cos 45^{\circ}; \text{ and } \cos op = \frac{\cos 54^{\circ} 44' \cos (63^{\circ} 26' - \theta)}{\cos \theta},$$
$$\theta = 45^{\circ}. \qquad \qquad \qquad op = 39^{\circ} 14'.$$

To find the second, namely,  $o=(111):p=(210)$ , we can use the right-angled triangle  $opd=(111):(210):(110)$  (the letter  $d$  not being given on the projection as the face (110) is not developed), in which we know that  $od$  is  $35^{\circ} 16'$  (half the octahedron angle between (111) and (11 $\bar{1}$ )), that  $dp$  is  $45^{\circ} - 26^{\circ} 34' = 18^{\circ} 26'$ , and that the angle between them at  $d$  is a right angle. From the Napierian diagram we derive :

$$\cos op = \cos 18^{\circ} 26' \cos 35^{\circ} 16'$$
$$op = 39^{\circ} 14'.$$

We thus see that both the angles under consideration between the primary  $o$ -face (111) and different adjacent  $p$ -faces are  $39^{\circ} 14'$ , the exact value of the angle as measured. This is in complete accordance with the symmetry of class 30 of the cubic system, and the proof now achieved brings to an end our morphological investigation of the crystal.

The results are printed in concise form in the following statement :

Table of Results for Cobaltite, CoAsS.

**Crystal-System :** Cubic. **Class :** 30, pyrites class, parallel-faced hemihedral or tesserall central class.

**Habit :** Approximately spherical, due to more or less equal development of triangular faces of pyritohedron and octahedron, and blunting of pyritohedron edges by cube-face strips.

**Forms observed :** Cube  $c=\{100\}$ , octahedron  $o=\{111\}$ , and pentagonal dodecahedron  $p=\{210\}$  (pyritohedron). Two latter predominate, octahedron somewhat the more prominently. Cube faces narrow, sometimes mere strips, and the adjacent faces of  $\{210\}$  are striated parallel to the strips.

**Interfacial angles :** as given in the following table.

MORPHOLOGICAL ANGLES OF COBALTITE.

Angle.	No. of Measurements.	Limits.	Mean observed.	Calculated.	Difference.
$\left\{ \begin{array}{l} cc=(100):(010) \\ cp=(100):(210) \\ pc=(210):(010) \end{array} \right. \begin{array}{l} . \\ . \\ . \end{array}$	<div>12</div> <div>12</div> <div>12</div>	<div>89° 55'–90° 7'</div> <div>26 31–26 37</div> <div>63 20–63 31</div>	<div>90° 0'</div> <div>26 34</div> <div>63 26</div>	<div>90° 0'</div> <div>26 34</div> <div>63 26</div>	<div>0'</div> <div>0</div> <div>0</div>
$\left\{ \begin{array}{l} co=(001):(111) \\ \text{or } (100):(111) \\ oo=(111):(1\bar{1}\bar{1}) \\ \text{or } (111):(\bar{1}\bar{1}1) \end{array} \right. \begin{array}{l} . \\ . \\ . \\ . \end{array}$	<div>24</div> <div>12</div>	<div>54 41–54 48</div> <div>70 31–70 33</div>	<div>54 44</div> <div>70 32</div>	<div>54 44</div> <div>70 32</div>	<div>0</div> <div>0</div>
$\left\{ \begin{array}{l} pp=(210):(021) \\ \text{or } (210):(102) \end{array} \right. \begin{array}{l} . \\ . \end{array}$	<div>10</div>	<div>66 19–66 29</div>	<div>66 25</div>	<div>66 25</div>	<div>0</div>
$\left\{ \begin{array}{l} op=(111):(102) \\ \text{or } (111):(210) \end{array} \right. \begin{array}{l} . \\ . \end{array}$	<div>12</div>	<div>39 11–39 18</div>	<div>39 14</div>	<div>39 14</div>	<div>0</div>

Owing to the excellence of the faces of this crystal, and the consequent clear definition of the signal images, the agreement between the observed and calculated angles is exceptionally good.



## CHAPTER XII

### TETRAGONAL SYSTEM

**Three rectangular crystallographic axes, two being equal and lying in the horizontal plane, the third being vertical. Characteristic of system, one tetragonal symmetry axis.**

THE tetragonal system includes seven classes, the lowest of which in order of symmetry possesses only the minimum essential of the system, namely, the tetragonal axis of symmetry. This latter is identical in direction with the vertical (the third and singular) crystallographic axis, the two equal crystallographic axes being arranged equatorially.

The seven classes are derived in a manner which arranges them in three groups of two, two, and three classes respectively.

The first two classes possess only the tetragonal axis of symmetry, but in the one case it is of simple, and in the other of compound symmetry. In the latter case we have class 10, the stereographic projection of which as regards elements of symmetry and the general form  $\{hkl\}$  has already been shown in Fig. 77, which is here repeated in Fig. 137 ;

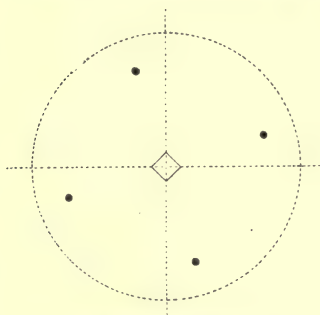


FIG. 136.—Class 9.

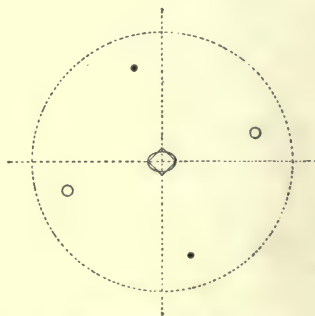


FIG. 137.—Class 10.

and in the former case we have class 9, represented in stereographic projection in Fig. 136. The effect of the symmetry being only compound in class 10 is to render the tetragonal axis only equivalent to a digonal axis of simple symmetry, the reflection across the equatorial plane which

accompanies the operation of the tetragonal axis, rotation for  $90^\circ$ , causing two of the poles of the general form to be thrown into the lower hemisphere, thus producing a bisphenoidal solid represented by two poles in each hemisphere, arranged alternately to each other. In class 9, where the symmetry is simple tetragonal, the four poles are situated in the same hemisphere, and the tetragonal axis is thus of polar character, and the faces developed on the crystal at the two ends of the vertical axis may consequently belong to quite different forms.

If we add to the single element of symmetry exhibited in classes 9 and 10 a digonal axis in the equatorial plane, the four additional poles introduced by its operation are found to be also symmetrical to a second digonal axis at right angles to the first, the two being coincident with the horizontal crystallographic axes; two new classes, 11 and 14, are thus produced, the stereographic projections of which are given in Figs. 138 and 139. In class 14 it is found that the disposition of faces brought about by the operation of these further elements of symmetry is such



Fig. 138.—Class 11.

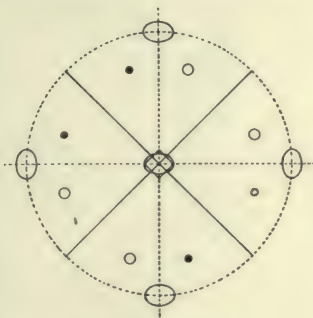


Fig. 139.—Class 14.

that there is also symmetry about two vertical planes intersecting in the tetragonal axis, and bisecting the angles between the two vertical crystallographic axial planes. In class 11 no symmetry planes are developed by the addition of the two rectangular digonal axes, but there is symmetry also produced about another pair of digonal axes, bisecting the angles between those already added.

Three further classes are then derived from class 9, which possesses the minimum of truly tetragonal symmetry, namely the tetragonal axis of simple symmetry itself, by the addition of a plane of equatorial symmetry (class 12), a vertical plane of symmetry (class 13), or both (class 15). In the case of class 12 the addition of the equatorial plane of symmetry perpendicular to the tetragonal axis simply results in removing the polar character of that axis, the two ends of the crystal, upper and lower, being now symmetrical. Its stereographic projection is given in Fig. 140. In class 13 (Fig. 141) the addition of a plane of symmetry parallel to the vertical axis causes the repetition of each of the four poles of the general form  $\{hkl\}$  across that symmetry plane, and the effect is to make the crystal and its projection symmetrical

also about three other planes of symmetry also parallel to the vertical

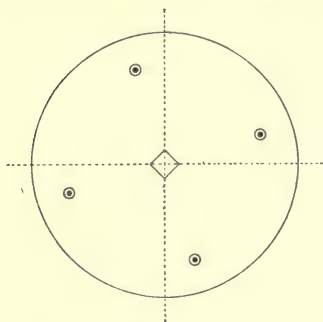


FIG. 140.—Class 12.

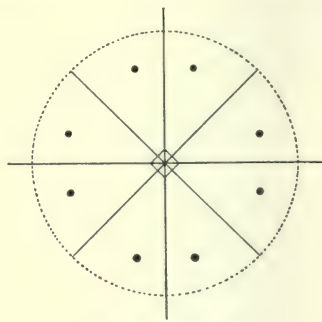


FIG. 141.—Class 13.

tetragonal axis and intersecting each other and the first plane in it, the four planes being arranged at  $45^\circ$  from each other.

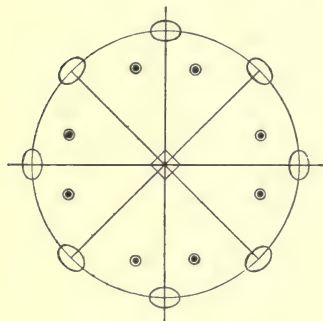


FIG. 142.—Class 15.

Finally, by combining classes 12 and 13, or in other words, adding to class 9 both the equatorial plane and the four vertical symmetry planes, we find that the effect is also to cause the presence of four digonal axes where the four vertical planes intersect the equatorial plane, and thus we have combined in this class, 15, represented in Fig. 142, the whole of the elements of symmetry possible in the tetragonal system. Class 15 is, therefore, the holohedral class, or class of highest tetragonal symmetry.

It will be observed that the tetragonal axis is polar only in classes 9 and 13, so that these classes are the hemimorphic ones.

*Class 15.—Ditetragonal-Bipyramidal Class. Holohedral Class.  
Type, Ditetragonal Equatorial.*

The crystals of this highest class of tetragonal symmetry are distinguished, as above indicated, by possessing the one essential tetragonal axis, and 4 symmetry planes (of which two are crystallographic axial planes) intersecting in it, thus rendering it a ditetragonal axis, and which are arranged at  $45^\circ$  to each other; there is also a fifth equatorial plane of symmetry perpendicular to the others and to the tetragonal axis, and there are consequently also 4 digonal (di-digonal) axes lying in this equatorial plane, at its intersection with each of the 4 other symmetry planes. These elements of symmetry are clearly shown by the stereographic projection given in Fig. 142, the plane of projection being



the equatorial plane, which forms the third crystallographic axial plane; the tetragonal axis is represented by the pole in the centre. The two vertical crystallographic axial planes are represented by the back-to-front and right-and-left diameters. There are seven forms in this holohedral class, which will be considered in turn.

(1) **The basal pinakoid,  $\{001\}$ .** The form  $\{100\}$  does not, as in the cubic system, include the six faces parallel to the crystallographic axial planes, the different nature of the vertical axis now causing these faces to be divided into two forms, consisting of the four vertical faces in one case and the two horizontal ones in the other, which latter is now under consideration. Hence, this form is an open one consisting only of the two parallel faces  $(001)$  and  $(00\bar{1})$ , and is, therefore, termed the basal pinakoid (see page 59 for derivation and exact meaning of the term "pinakoid"). Its pole occupies the centre of the projection (Fig. 156), and may be considered as the special form produced when the general pole  $(hkl)$ , situated inside the primary triangle (Fig. 142) in the projection formed by two adjacent digonal axial radii and the  $45^\circ$ -segment of the primitive circle which they cut off, migrates to that corner of the triangle which occupies the centre of the projection, where the digonal axes intersect.

(2) **Tetragonal prism of the first order,  $\{110\}$ ,** also called **protoprism**. This form is also an open one like the basal pinakoid, but consists of four faces,  $(110)$ ,  $(1\bar{1}0)$ ,  $(\bar{1}10)$ , and  $(11\bar{0})$ , which are parallel to the two vertical planes of symmetry bisecting the angles between the two vertical crystallographic axial planes, and the edges of intersection of which are parallel to the vertical axis. The poles of the four faces are consequently situated on the primitive circle at the ends of the diameters arranged at  $45^\circ$  to the axial diameters. The faces thus make equal intercepts on the horizontal crystallographic axes  $a$  and  $b$ , represented in the projection by the axial diameters just referred to parallel respectively to the longer and shorter edges of the page,  $a$  running back and front and  $b$  laterally right and left. It will be obvious that, given one such pole at the intersection of one of the  $45^\circ$ -diameters with the primitive circle, the symmetry demands that there shall be three others, by repetition over the crystallographic axial planes of symmetry. This form may be considered as the special case which occurs when the general pole  $(hkl)$  migrates to that corner of the primary triangle of the projection which is formed by the intersection of an interaxial diameter with the primitive circle. With the basal pinakoid end faces, this form makes a closed rectangular prism, of square horizontal section, and only differing from the cube by the elongation or shortening of the vertical dimension.

It is represented as thus closed in Fig. 143. The axes employed in this and the succeeding tetragonal figures are those of an actual tetragonal substance, anatase, for which the axial ratio of the two equal horizontal axes to the vertical axis is  $a : c = 1 : 1.7771$ .

(3) **Tetragonal prism of the second order,  $\{100\}$ .** When the faces of the tetragonal prism are parallel to the vertical crystallographic axial planes, as in the case of the vertical cube faces, we have this second variety of tetragonal prism of square section produced, identical in shape with that of the first order and differing only in position. The poles of the form are situated at the points of intersection of the primitive circle and the crystallographic axial diameters, so that the form may be considered as the special case produced when the general pole  $(hkl)$  migrates to this corner of the primary  $45^\circ$ -triangle. The front face is  $(100)$ , the back face parallel to it  $(\bar{1}00)$ , the right-hand side

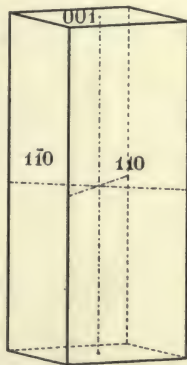


FIG. 143.—First Order Tetragonal Prism.

face is (010), and the left-hand face parallel to it is (0 $\bar{1}$ 0). The form as closed by the basal pinakoid is shown in Fig. 144. In an actual crystal showing both forms of tetragonal prism, or different crystals showing them separately, there will usually be surface markings, striations, or other physical differences to distinguish the two from one another.

(4) **Ditetragonal prism,  $\{hk0\}$ .** Any face the pole of which is situated on the primitive circle (that is, which is parallel to the vertical crystallographic axis), in any position other than at the intersection with one of the 4 principal diameters shown in the projection, Fig. 142, must, by reason of the symmetry of this class 15, be repeated over each of the 4 symmetry planes represented by those diameters, so as to form an

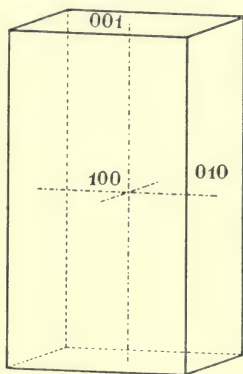


FIG. 144.—The Second Order Tetragonal Prism.

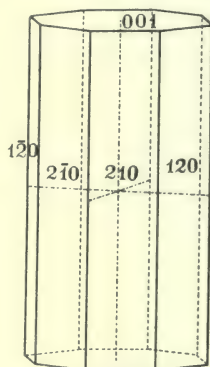


FIG. 145.—The Ditetragonal Prism.

eight-sided prism, which has always a section showing two alternating kinds of angles, a less and a greater. For the case where the pole would be half-way between any two principal diameters is an impossible one, corresponding to irrational values of the first two indices, their ratio being  $= \tan 22\frac{1}{2}^\circ = 2.4142$ . A truly regular octagonal prism is a frequent natural occurrence on tetragonal crystals, but it is always a combination of the first and second order prisms  $\{110\}$  and  $\{100\}$  showing the physical differences already alluded to. The ditetragonal prism  $\{210\}$  is shown in Fig. 145, combined with the basal plane. It may be considered as the special case produced when the general pole ( $hkl$ ) migrates on to the primitive circle, but not at an intersection with an axis, that is, on to the 45°-segmental side of the primary triangle.

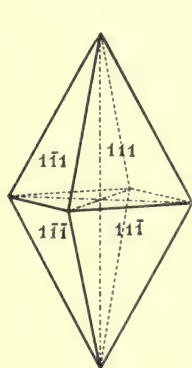


FIG. 146.—First Order Tetragonal Bipyramid.

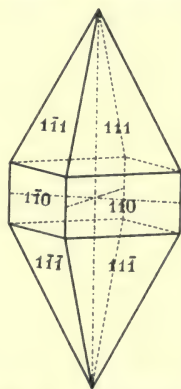


FIG. 147.—Combination of First Order Prism and Pyramid.

and that of the first order prism  $\{110\}$ , the form produced is a four-sided pyramid, each face making equal intercepts on the two horizontal axes. When this form is chosen as the parametral form the symbol is  $\{111\}$ , otherwise the symbol is of the general type

$\{hhl\}$ , the first two indices being invariably equal. Each pole on the projection now represents two faces, one in the upper hemisphere and the other in the lower hemisphere, the pyramid being thus a double one or "bipyramid" pointing upwards and downwards, the two pyramids being mutually joined in, and springing from, a square base occupying the central plane of the solid. It is illustrated in Fig. 146, and adjoining it in Fig. 147 is a drawing illustrating its combination with, and the truncation of its edges by, a prism likewise of the first order. Indeed the prism is the limiting case when the intercept on the  $c$  axis becomes increased to infinity, and the faces consequently become parallel to  $c$ ; the indices then become  $\{hh0\}$ , or to give them their simplest form  $\{110\}$ . Similarly, if the intercept on the vertical axis become likewise rationally reduced, we have as the limiting case of reduction to 0, the production of the basal pinakoid  $\{001\}$ , parallel to the two horizontal axes. In the first case the pyramid becomes longer and sharper, with increasing dihedral angle over the basal edges, the  $l$  index becoming less and less in comparison with  $h$ ; while in the latter case the pyramid becomes shorter and flatter, with diminishing angle over the basal edges, and a greater and greater  $l$  index as compared with  $h$ .

(6) **Tetragonal bipyramid of the second order,  $\{h0l\}$ .** When the pole of a face lies on the  $90^\circ$ -arc between  $(001)$  and  $(100)$ , represented by a crystallographic axial plane

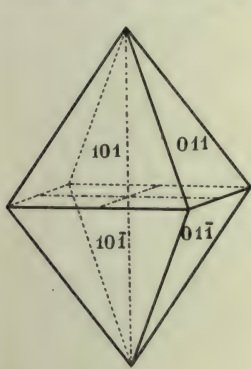


FIG. 148.—The Second Order Tetragonal Bipyramid.

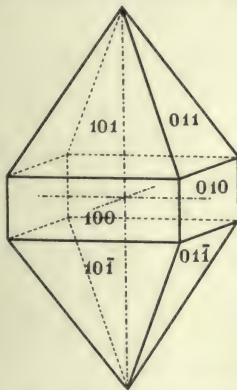


FIG. 149.—Combination of Second Order Prism and Pyramid.

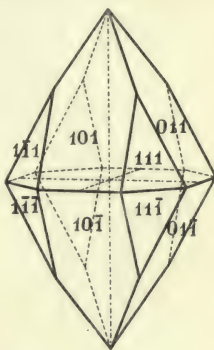


FIG. 150.—Combination of First and Second Order Bipyramids.

semi-diameter of the projection, a four-faced pyramid is again produced, by the repetition of the pole on the other three similar arcs as demanded by the symmetry of the class, and this being duplicated on the lower hemisphere gives us the tetragonal bipyramid of the second order, which is also a double square-based pyramid like that of the first order. Any face, however, will always be parallel to one of the horizontal crystallographic axes, and will consequently have a 0 in its symbol. When the intercepts are the parametral ones on the other two axes, the symbol is  $\{101\}$ . This form is shown in Fig. 148. The second order prism  $\{100\}$  forms the limiting case of increase of the vertical intercept, and the basal pinakoid  $\{001\}$  again forms the limiting case of shortening. In the four succeeding illustrations are exhibited several combinations of simple tetragonal forms. In Fig. 149 a tetragonal bipyramid of the second order with the prism of the same order truncating the basal edges is shown. In Fig. 150 a combination of the two primary tetragonal bipyramids of the two different orders  $\{111\}$  and  $\{101\}$  is represented. Fig. 151 portrays a combination of two bipyramids of the same order but having different values of the  $l$  index,  $\{111\}$  and  $\{112\}$ . And in Fig. 152 is represented the primary bipyramid of



the first order combined with the primary prism of the second order and the basal pinakoid.

(7) The last holohedral form of the tetragonal system is the general one  $\{hkl\}$ , the poles of which occupy the interior of the elementary spherical triangles, in positions which are symmetrical to the 4 planes of symmetry represented by the four diameters at  $45^\circ$ , as shown on the stereographic projection in Fig. 153, which is a repetition of Fig. 142, and represents the poles of one of the possible forms  $\{312\}$  of anatase, as well as the elements of symmetry. It is the 16-faced ditetragonal bipyramid, the appearance of which is represented in Fig. 154, the particular one shown being  $\{212\}$ . As its name implies it is a doubly terminated pyramid the basal section of which is eight-sided but not a regular octagon, although the sides are of equal length; it resembles the ditetragonal prism in section, and indeed that form may be regarded as the limiting case of a ditetragonal bipyramid of infinite vertical intercept. The section of both prism and pyramid shows alternately larger and

FIG. 151.—Combination of Two First Order Bipyramids.

smaller angles. The angles over the basal edges of the ditetragonal bipyramid are, however, all equal, just as are those of the simple pyramids of the first and second orders. As already explained in connection with the prism, a ditetragonal

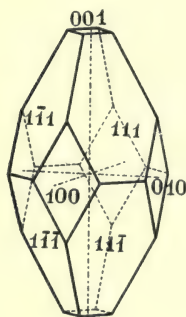


FIG. 152.—Combination of First Order Bipyramid, Second Order Prism, and Basal Pinakoid.

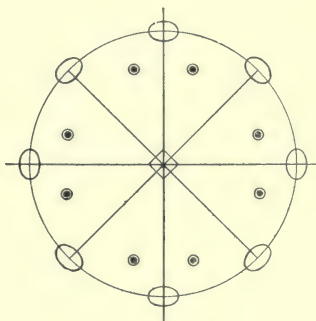


FIG. 153.  
Symmetry Elements and General Form of Class 15.

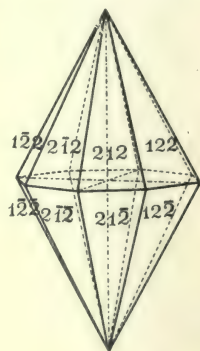


FIG. 154.  
The Ditetragonal Bipyramid.

pyramid the base of which is a regular octagon is impossible on account of irrationality. The actual angles over the pyramidal edges resemble the section in exhibiting alternately larger and smaller values. This general form of the tetragonal system, possessing the fullest symmetry appertaining to that system, passes into a simple pyramid of the first order when  $h=k$ , the two faces from each octant then coalescing into the same plane making equal intercepts on the two horizontal crystallographic axes. It passes into the pyramid of the second order when  $k=0$  in the form symbol  $\{hkl\}$ , a face from each of every two adjacent octants coalescing to form a plane parallel to one of the horizontal crystallographic axes. Finally, if either of these limiting cases is also accompanied by the extension of the intercept on the vertical axis to infinity, the prism of the corresponding order is produced, or if the vertical intercept becomes 0 the ditetragonal bipyramid passes into the basal pinakoid. In all these cases of the evolution of one form from another, it must be remembered that the passage occurs in definite steps, corresponding to specific stages

or cases of rationality of the indices  $h, k, l$ , and not by very gradual changes of almost insensible magnitude. This completes the detailed study of the holohedral class 15 of tetragonal crystals. The following is a summary of the seven types of forms:

*List of Forms in Class 15.*

- {001} Basal pinakoid. 2 faces.
- {110} Tetragonal prism of first order. 4 faces.
- {100} Tetragonal prism of second order. 4 faces.
- { $hk0$ } Ditetragonal prism. 8 faces.
- { $hhl$ } Tetragonal bipyramid of the first order, including the primary parametral form {111}. 8 faces.
- { $h0l$ } Tetragonal bipyramid of the second order, including the primary one {101}. 8 faces.
- { $hkl$ } Ditetragonal bipyramid. 16 faces.

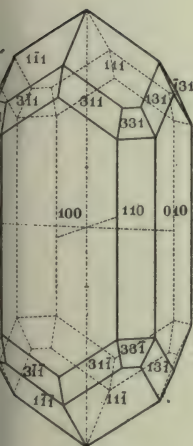


FIG. 155.—Zircon.

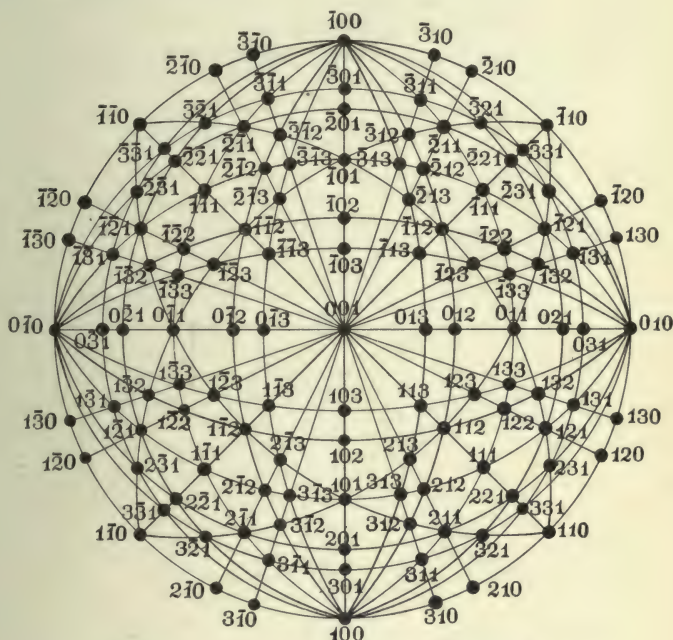


FIG. 156.—Stereographic Projection of Tetragonal Forms.

In actual practical work the discrimination between first and second order prisms and pyramids is not possible, unless both forms are developed on the crystal. For rotation of either for  $45^\circ$  converts it into the other, and even when both are present it is only possible to decide arbitrarily which is to be considered as of the first order and which of the second. No ambiguity can, however, arise as to which is the vertical axis, on account of the unmistakable particular character of this axis, which is often termed the principal axis, and which will subsequently be shown to confer on the crystal optical properties of a unique character, which render any mistake in recognising it out of the question.

Excellent examples of substances crystallising in the ditetragonal-bipyramidal class are zircon, silicate of zirconium,  $\text{ZrSiO}_4$ , cassiterite or tin-stone, dioxide of tin,  $\text{SnO}_2$ , and the two tetragonal forms of titanium dioxide,  $\text{TiO}_2$ , both of which, rutile and anatase, belong to this class yet exhibit different forms. A fairly complicated crystal of anatase will be thoroughly worked out in the next chapter. Titanium dioxide is trimorphous, a third rhombic variety, brookite, being a well-known and optically very interesting mineral, the optical characters of which will be described in Chapter XLIX. A characteristic crystal of zircon is shown in Fig. 155, on which are developed the forms  $\{100\}$ ,  $\{110\}$ ,  $\{111\}$ ,  $\{331\}$ , and  $\{311\}$ . The axial ratio  $a : c = 1 : 0.6404$ .

In Fig. 156 is given a stereographic projection showing a considerable number of the commoner forms of tetragonal crystals, constructed for the axial ratio of anatase,  $a : c = 1 : 1.7771$ . The author has found it of the greatest practical help in the investigation of tetragonal crystals.

*Class 14.—Scalenohedral Class. Sphenoidal-Hemihedral Class.  
Type, Ditetragonal Alternating.*

This class corresponds to the hexakis-tetrahedral class 31 of the cubic system. The elements of symmetry are shown in the stereographic projection Fig. 157, which is Fig. 139 repeated here for convenience of reference. The three axial planes are no longer

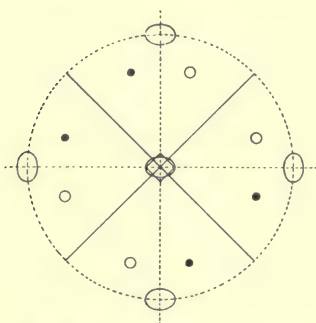


FIG. 157.—Symmetry Elements and General Form of Class 14.

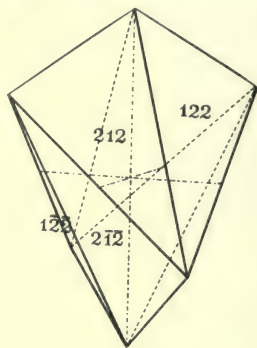


FIG. 158.  
The Tetragonal Scalenohedron.

planes of symmetry, the two vertical interaxial planes of symmetry alone persisting; the two horizontal digonal axes which formed the intersections of these latter planes with the equatorial plane also disappear, leaving only the two other digonal axes (the horizontal crystallographic axes) persisting. The main axis coincident with the vertical crystallographic axis remains tetragonal, however, and although the equatorial plane is no longer a plane of simple symmetry, it is one of compound symmetry, so that the tetragonal axis is one of alternating symmetry, or a tetragonal mirror-axis as it is variously called. This will become clear from a consideration of the general form of the class, which will be immediately proceeded to.



The **scalenohedron**,  $\{hkl\}$ , is an eight-faced solid the poles of which are shown in the projection in Fig. 157. Fig. 158 represents the scalenohedron  $\{212\}$ . As will be evident from that projection there are two modifications possible, the second being obtained by changing the dots on the projection into rings and *vice versa*. The two forms are not, however, different solids; they differ only in position while *in situ*, and rotation of either for  $90^\circ$  about the vertical axis produces the other. The two forms are the positive,  $\{hkl\}$ , shown in Fig. 158, and the negative,  $\{\bar{h}\bar{k}\bar{l}\}$ . That the principal axis is a tetragonal one of alternating symmetry is shown by the fact that each pole on the projection if rotated  $90^\circ$  about that axis and then immediately reflected over the equatorial plane will coincide with the pole of another face on the same scalenohedron. And yet in spite of this reflection there is no centre of symmetry, and this fact has been shown by Fedorov to displace the "centre of symmetry" from the position in which it has long been regarded as a true element of symmetry, for it only accompanies the operation of a plane of compound symmetry in two special cases, which have been referred to in Chapter IX.

The solid angles at the poles of the principal axis are each formed by the meeting of four edges in two pairs, one pair long and acutely inclined and the other pair short and obtusely inclined; the other four edges are of intermediate length. These three kinds of edges correspond to three different interfacial angles, of which that over any pair of long edges is the same as the angle over the pyramidal edges of the holohedral ditetragonal bipyramid.

There is only one further new solid introduced into the tetragonal system by the operation of class 14 symmetry, namely the double-wedge-shaped **bisphenoid** (from  $\sigma\phi\eta\nu$ —a *wedge*),  $\{hhl\}$ , which may be regarded as derived from the bipyramid of the first order, just as the scalenohedron may be considered to be derived from the ditetragonal bipyramid. The primary form  $\{111\}$  of this solid is illustrated in Fig. 159, and is formed when the pair of facial poles adjacent and symmetrical to one of the  $45^\circ$  (interaxial) planes of symmetry coalesce into one lying in the plane itself, which is expressed in the actual form of the solid by the further flattening into a plane of the two faces on either side of the long edges of the scalenohedron, which in the latter solid meet in that edge to form a very flat ridge.

Each face of the bisphenoid is an isosceles triangle, and the whole solid resembles a tetrahedron, but drawn out, or compressed, according to the value of the axial ratio  $a : c$ , along the direction of the principal (tetragonal) axis. There are two forms of the bisphenoid as of the scalenohedron, the positive  $\{hhl\}$ , shown *in situ* in Fig. 159, and the negative  $\{\bar{h}\bar{h}\bar{l}\}$ , but the two are superposable when rotated  $90^\circ$  out of their positions of derivation from the holohedral pyramid of the first order,  $\{hhl\}$ . Hence there is only one such solid.

The other forms consistent with the symmetry of this class are all identical with the holohedral forms already described in class 15, the two differences from that class being as we have seen that 2 holohedral forms, the first order bipyramid and the ditetragonal bipyramid, are replaced by the bisphenoid and scalenohedron respectively. The basal pinakoid is the same by virtue of the operation of either of the digonal axes. All three prisms are the same because the general poles of both hemispheres have a prism as their limiting form when they migrate to the primitive circle, a first or second order prism if they go to the ends of the interaxial or axial diameters, and a ditetragonal prism if they go elsewhere on the circle. The tetragonal pyramid of the second order is the same as the holohedral one because when each pair of the general poles migrate to the crystallographic axial diameters

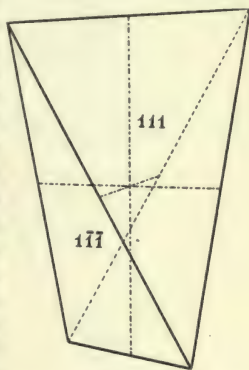


FIG. 159.  
The Tetragonal Bisphenoid.

they do so by increasing their separation, one pole going to each semi-diameter; whereas the tetragonal pyramid of the first order becomes the bisphenoid by the coalescence of each pair of poles of the same hemisphere on one half of one and the same interaxial diameter, those of the upper hemisphere on one diameter and those of the lower on the other. We have, therefore, the following seven forms to tabulate as belonging to this class :

*List of Forms in Class 14.*

- {001} Basal pinakoid. 2 faces.
- {110} Tetragonal prism of the first order. 4 faces.
- {100} Tetragonal prism of the second order. 4 faces.
- {hkl} Ditetragonal prism. 8 faces.
- {hhl} Positive tetragonal bisphenoid of the first order, including the primary form {111};  $\{\bar{h}hl\}$  negative tetragonal bisphenoid of the first order, including the primary form  $\{\bar{1}\bar{1}1\}$ . Each 4 faces.
- {hol} Tetragonal bipyramid of the second order, including the primary form {101}. 8 faces.
- {hkl} Positive tetragonal scalenohedron;  $\{\bar{h}kl\}$  negative tetragonal scalenohedron. Each 8 faces.

An excellent natural example of a substance crystallising in this class is the common ore of copper, chalcopyrite, copper pyrites,  $\text{CuFeS}_2$ , a typical crystal of which, showing faces of the two bisphenoids {111} and  $\{\bar{1}\bar{1}1\}$ , the former much more developed than the latter, in combination with the prism of the first order {110}, the bipyramid of the second order {101}, and the basal pinakoid {001}, is given in Fig. 160. The ratio of the axes is :  $a : c = 1 : 0.9856$ .

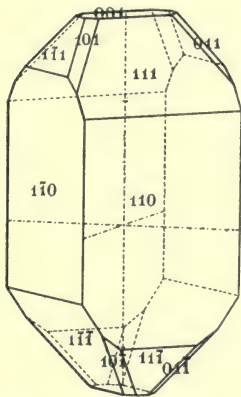


FIG. 160.—Copper Pyrites.

Among artificial chemical preparations potassium hydrogen phosphate,  $\text{KH}_2\text{PO}_4$ , affords an example, readily procurable in good crystals of some size, or as growing crystals on a microscope slide suitable for screen projection; but as a rule the forms present are those which are identical with the holohedral forms of the tetragonal system (the second order prism {100} and bipyramid {101} chiefly), and it is only by the character of the etched figures on these faces that the hemihedrism or prevalence of class 14 symmetry is indicated. The observation by Mitscherlich in the year 1819, that the analogous arsenate  $\text{KH}_2\text{AsO}_4$ , and the two corresponding ammonium salts  $\text{NH}_4 \cdot \text{H}_2\text{PO}_4$  and  $\text{NH}_4 \cdot \text{H}_2\text{AsO}_4$ , also crystallise in tetragonal forms similar to those of this salt, was the direct means of his discovery of the principle of isomorphism.

*Class 13.—Ditetragonal-Pyramidal Class. Hemimorphic-Holohedral Class. Type, Ditetragonal Polar.*

In this class the tetragonal axis and the four symmetry planes intersecting in it operate as in the holohedral class 15, but all other elements of symmetry, including the equatorial plane, disappear entirely. The elements are shown in the projection, Fig. 161.

The general form  $\{hkl\}$  is also shown by its poles on the projection, and is the upper open half of a ditetragonal bipyramid. If rings were given instead of dots it would equally well represent the lower half. The two halves, however, are never necessarily both present on a crystal of this class, owing to the absence of the equatorial plane of symmetry, the tetragonal axis being thus polar. The figure may be closed by one face of the basal plane, the two parallel basal pinakoid faces of the holohedral class belonging in this class to two separate forms,  $\{001\}$  and  $\{00\bar{1}\}$ . The general form is thus the **ditetragonal pyramid**, of which there are these two, upper and lower, modifications, the upper or upwards pointing form (represented by the upper half of Fig. 154) being the positive  $\{hkl\}$  and the lower or downwards pointing form (the lower half of Fig. 154) being the negative  $\{h\bar{k}l\}$ . No changes are produced in the exterior appearance of the tetragonal prisms by the operation only of this lower degree of symmetry of class 13. For the prisms are equally produced by the migration to the primitive circle of poles in either the upper or the lower hemisphere.

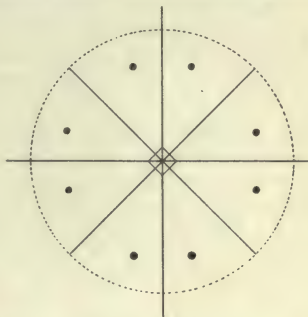


FIG. 161.—Symmetry Elements and General Form of Class 13.

But the bipyramids of the two orders are affected similarly to the ditetragonal bipyramid, of which indeed they are only special cases, that of the first order being the special case when  $k=h$ , and that of the second order being the case when  $k=0$ ; the graphic interpretation being the migration of the general pole  $\{hkl\}$ , situated within the  $45^\circ$ -triangle of the diameters representing the great zone circles of the holohedral vertical symmetry planes, to one or other of these zone circles themselves. In both cases the operation of class 13 symmetry causes the upper (upwards pointing) and lower (downwards pointing) pyramids to become two separate forms, the positive  $\{hhl\}$  or  $\{h0l\}$  (upper halves of Figs. 146 and 148), and the negative  $\{h\bar{h}l\}$  or  $\{h0\bar{l}\}$  (lower halves of Figs. 146 and 148).

As the two faces  $\{001\}$  and  $\{00\bar{1}\}$  of the holohedral basal pinakoid are now separate one-face forms, each may appropriately be termed a "**pedion**" (from  $\pi\epsilon\delta\iota\omicron\nu$ —a plane).

In résumé, the following forms are included in this class :

*List of Forms in Class 13.*

- $\{001\}$  Upper positive basal plane or pedion ;  $\{00\bar{1}\}$  lower negative basal plane or pedion. Each 1 face.
- $\{110\}$  Tetragonal prism of the first order. 4 faces.
- $\{100\}$  Tetragonal prism of the second order. 4 faces.
- $\{hk0\}$  Ditetragonal prism. 8 faces.
- $\{hhl\}$  Upper positive tetragonal pyramid of the first order ;  $\{h\bar{h}l\}$  lower negative tetragonal pyramid of the first order. Each 4 faces.
- $\{h0l\}$  Upper positive tetragonal pyramid of the second order ;  $\{h0\bar{l}\}$  lower negative tetragonal pyramid of the second order. Each 4 faces.
- $\{hkl\}$  Upper positive ditetragonal pyramid ;  $\{h\bar{k}l\}$  lower negative ditetragonal pyramid. Each 8 faces.

The absence of centro-symmetry in this class is well shown by crystals of iodosuccinimide,  $C_4H_4O_2NI$ , first described by von Groth and subsequently by Traube, and an illustration of one of which, prepared by Traube and figured by him on p. 579 of his memoir



(*Zeitschr. für Kryst.* 23, 577), is given in Fig. 162. The upper and lower terminations of the first order prism  $m=\{110\}$  are seen to be formed by two different pyramids, the primary positive  $\{111\}$ , and  $\{22\bar{1}\}$ . The presence also of small faces of the complementary pyramidal form  $\{221\}$  might be thought to indicate holohedrisism, but the complementary primary negative pyramid  $\{1\bar{1}1\}$  is not similarly present. Moreover, the etched figures obtained on the faces of the prism  $m=\{110\}$  also indicate clearly the hemimorphic character of the crystals and the absence of the equatorial plane of symmetry. The two ends also exhibit opposite pyroelectrical characters, the upper blunter end being positive and the lower sharper end negative, which affords a further strong confirmation of the supposition that the substance belongs to this class. The axial ratio of the crystals, according to von Groth, is :  $a : c = 1 : 0.8733$ .

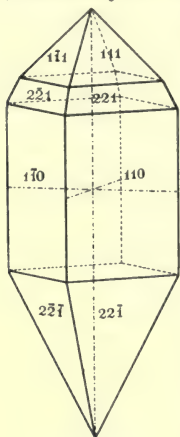


FIG. 162.  
Iodosuccinimide.

*Class 12.—Bipyramidal Class. Pyramidal Hemihedral Class.*  
*Type, Tetragonal Equatorial.*

This class of tetragonal crystals is distinguished by possessing only the tetragonal axis and the equatorial symmetry plane perpendicular to

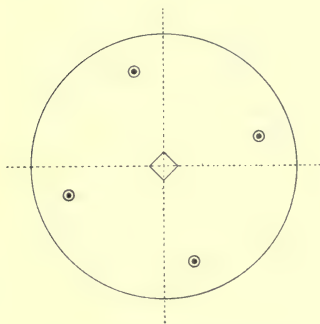


FIG. 163.—Symmetry Elements  
and General Form of Class 12.

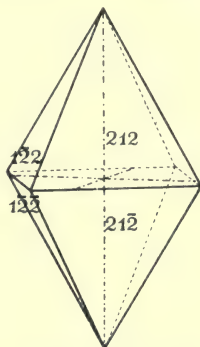


FIG. 164.—Third Order  
Tetragonal Bipyramid.

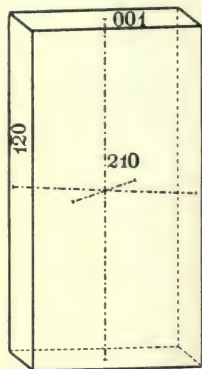


FIG. 165.—Third Order  
Tetragonal Prism.

it. Both the primary and secondary planes of symmetry parallel to the axial vertical planes and at  $45^\circ$  to them disappear, and with them the four digonal horizontal axes. The stereographic projection in Fig. 163 shows both the symmetry elements and the general form  $\{hkl\}$ .

This latter is a tetragonal bipyramid composed of four pairs of parallel faces, there being centro-symmetry present ; it is indistinguishable as regards outward shape from the other two kinds, the first and second orders, of tetragonal pyramids. Its pole, however, falls neither on a crystallographic axial diameter nor on one at  $45^\circ$  thereto, but, as the projection indicates, somewhere in the triangle formed by those two types of diameter. It is, therefore, a **tetragonal bipyramid of the third order**. It is shown in

Fig. 164, the particular form being  $\{212\}$ . There are, however, two such forms having the same numbers in their indices, and the second variety can be obtained from the first modification  $\{hkl\}$  shown in the projection by rotating the solid about either of the crystallographic axes  $a$  or  $b$  for  $180^\circ$ . Its symbol would have the  $h$  and  $k$  values of the first modification interchanged, and can be written therefore as  $\{khl\}$ . To these two forms belong two corresponding **tetragonal prisms of the third order**, the first of which is represented in Fig. 165, the form shown being  $\{210\}$  corresponding to the bipyramid drawn in Fig. 164. Their form symbols are  $\{hk0\}$  and  $\{kh0\}$ , and they may be considered as the limiting forms of the corresponding bipyramids when the poles migrate on to the primitive circle, and the intercept on the  $c$  axis becomes infinite, that is, the faces become parallel to that axis.

Other limiting cases are when  $k=0$  and when  $h=k$ , that is when the poles migrate to the two kinds of diameters of the projection, parallel to the edges of the page or (not shown in Fig. 163) at  $45^\circ$  thereto, when we obtain the ordinary second and first order bipyramids respectively, or if also  $l=0$  the corresponding prisms. The basal pinakoid  $\{001\}$  is also again the limiting form when any of the three bipyramids are flattened until their faces merge in a plane parallel to the  $a$  and  $b$  crystallographic axes.

We have, therefore, the following

*List of Forms in Class 12.*

- $\{001\}$  Basal pinakoid. 2 faces.
- $\{110\}$  Tetragonal prism of the first order. 4 faces.
- $\{100\}$  Tetragonal prism of the second order. 4 faces.
- $\{hk0\}$  Tetragonal prism (right-hand form) of the third order;  $\{kh0\}$  left-hand form of the same. The two solids indistinguishable. Each 4 faces.
- $\{hhl\}$  Tetragonal bipyramid of the first order. 8 faces.
- $\{h0l\}$  Tetragonal bipyramid of the second order. 8 faces.
- $\{hkl\}$  Tetragonal bipyramid (right-hand form) of the third order;  $\{khl\}$  left-hand form of the same. The two solids indistinguishable. Each 8 faces.

This class 12 is so characteristic of the symmetry of crystals of scheelite, tungstate of calcium,  $\text{CaWO}_4$ , that it is sometimes called the "scheelite class." In Fig. 166 is shown a crystal of scheelite which exhibits a combination of the predominating primary bipyramid of the second order  $\{101\}$ , with that of the first order  $\{111\}$ , and two bipyramids of the third order,  $\{313\}$  and  $\{131\}$ . The axial ratio of scheelite is  $a : c = 1 : 1.5359$ .

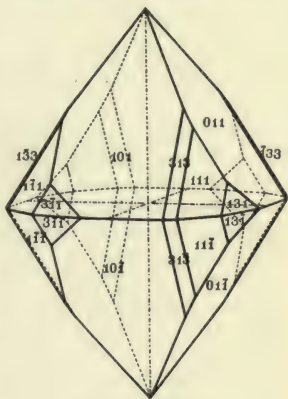


FIG. 166.—Scheelite.

*Class 11.—Trapezohedral Class. Trapezohedral-Hemihedral Class.*  
*Type, Tetragonal Holoaxial.*

This class possesses no symmetry planes at all, but all the symmetry axes of the system, namely, the tetragonal principal axis and the four digonal axes in the plane of the horizontal crystallographic axes, which are identical with two of them, the other two being at  $45^\circ$  to these two and thus bisecting their angles.

These symmetry elements and the general form  $\{hkl\}$  are shown in the stereographic projection, Fig. 167. This form is the only new solid introduced by the symmetry of this class, and is called the **tetragonal trapezohedron**, an eight-faced solid the four upper and four lower faces of which meet like those of a pyramid in polar edges intersecting in the principal axis at a more or less sharply pointed solid angle, the upper or lower termination of the bipyramid. It is at once distinguished from the tetragonal bipyramid, however, by the zig-zag arrangement of the eight alternately longer and shorter edges around the middle of the solid, a longer and a shorter edge going with every two polar edges to form the boundary of each face, which has thus the outline of a trapezoid. The shorter edges are bisected by the horizontal axes. There are two distinct enantiomorphous forms of this solid, shown in Figs. 168 and 169, the former

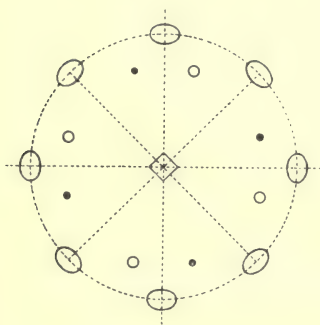


FIG. 167.  
Symmetry Elements and General  
Form of Class 11.

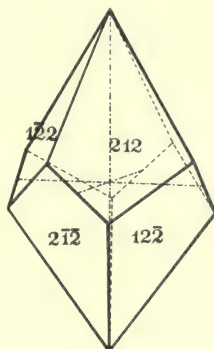


FIG. 168.  
Left Positive and Right Negative Tetragonal  
Trapezohedra.

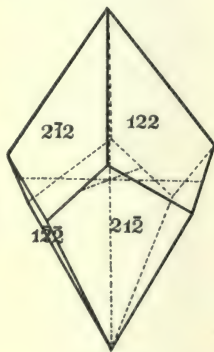


FIG. 169.

representing the left or positive form  $\{hkl\}$  and the latter the right negative modification  $\{khl\}$ , the particular trapezohedra being  $\{212\}$  and  $\{122\}$ ; the poles of the former are analogous to those shown in the projection Fig. 167 for  $\{312\}$ , and the poles of the other are obtained by exchanging the dots for rings and *vice versa*.

The two forms are truly enantiomorphous, that is, they cannot be brought to resemble each other by rotation.

The other forms possible to this combination of symmetry elements are identical with the holohedral forms in the cases of the basal pinakoid, prisms of the two orders, ditetragonal prism, and bipyramids of the two orders, as described in class 15. This fact can be readily verified by considering the effect of the corresponding migrations of the general poles, to the centre, to the primitive circle, or to the digonal-axial diameters, of the projection.

We have, therefore, the following forms to include in this class :

*List of Forms in Class 11.*

- $\{001\}$  Basal pinakoid. 2 faces.
- $\{110\}$  Tetragonal prism of the first order. 4 faces.
- $\{100\}$  Tetragonal prism of the second order. 4 faces.
- $\{hko\}$  Ditetragonal prism. 8 faces.
- $\{hhl\}$  Tetragonal bipyramid of the first order. 8 faces.
- $\{h0l\}$  Tetragonal bipyramid of the second order. 8 faces.
- $\{hkl\}$  Left positive tetragonal trapezohedron;  $\{khl\}$  right negative tetragonal trapezohedron. Two distinct enantiomorphous solids. Each 8 faces.

Sulphate of strychnine,  $C_{21}H_{22}N_2O_2 \cdot H_2SO_4 \cdot 6H_2O$ , is the best-known



example among the few substances crystallising according to this class of symmetry. It usually exhibits only the first order primary bipyramid  $\{111\}$  in combination with the basal pinakoid  $\{001\}$ , the axial ratio being  $a:c=1:3.312$ ; but both the crystals and their aqueous solution are optically active, and cleavage plates parallel to the basal plane afford etched figures with dilute hydrochloric acid which indicate clearly the trapezohedral nature of the symmetry.

*Class 10.—Bisphenoidal Class. Sphenoidal-Tetartohedral Class.  
Type, Tetragonal Alternating.*

This class is distinguished by the operation of the equatorial plane as a plane of compound symmetry only, in simultaneous co-operation with the tetragonal axis. That is, as will be clearer from Fig. 170 showing the stereographic projection of the two elements of symmetry and the general form  $\{hkl\}$ , repetition of the general face  $(hkl)$  occurs by a rotation of  $90^\circ$  about the tetragonal axis followed at once (without a face being produced at this stage) by reflection across the equatorial plane. The symmetry is such as would be produced if the planes of symmetry of the scalenohedral class 14 disappeared, together with the digonal axes.

The general form  $\{hkl\}$  is a solid which was also produced under the operation of scalenohedral class 14 symmetry, namely, the bisphenoid, already illustrated in Fig. 159. The bisphenoid here produced, however, is not of the first order, as in the case of class 14, but of the third order. This **tetragonal bisphenoid of the third order** has four modifications, indistinguishable after removal out of their positions of derivation. The first variety is the left positive form  $\{hkl\}$ , the poles of which are shown in the projection. The other three varieties all have the same numbers in their indices, and are the right positive  $(khl)$ , the right negative  $\{h\bar{k}l\}$ , and the left negative  $\{khl\}$ .



FIG. 170.—Symmetry Elements and General Form of Class 10.

Besides these four third order bisphenoids, two **bisphenoids of the first order** belong to this class; they are produced when the pole  $(hkl)$  migrates on to the  $45^\circ$  (diagonal) diameter and  $h=k$ , and are termed the positive,  $\{hhl\}$ , and the negative,  $\{h\bar{h}l\}$ . They may be regarded as derived from the first order pyramid. Similarly, when the general pole migrates on to a crystallographic axial diameter we have a pair of **bisphenoids of the second order** produced, the right  $\{h0l\}$ , and the left  $\{0kl\}$ , which may be considered as derived from the second order pyramid. When, however, the pole  $(hkl)$  moves on to the primitive circle we have a tetragonal prism  $\{hk0\}$  of the third order, of which there are two varieties, a right  $\{hk0\}$  and a left  $\{k\bar{h}0\}$ . The first order and second order prisms, and also the basal pinakoid, remain as in the holohedral class 15. The prisms are the limiting cases of bisphenoids of increasing steepness and diminishing third index in relation to the other two indices. The basal pinakoid, on the other hand, is the limit of all bisphenoids of increasing flatness and increasing third index.

There are, therefore, the following forms in this class:

*List of Forms in Class 10.*

- $\{001\}$  Basal pinakoid. 2 faces.  
 $\{110\}$  Tetragonal prism of the first order. 4 faces.  
 $\{100\}$  Tetragonal prism of the second order. 4 faces.  
 $\{h k 0\}$  Right tetragonal prism of the third order;  $\{k h 0\}$  left tetragonal prism of the third order. Each 4 faces.  
 $\{h h l\}$  Positive tetragonal bisphenoid of the first order;  $\{h \bar{h} l\}$  negative tetragonal bisphenoid of the first order. Each 4 faces.  
 $\{h 0 l\}$  Right tetragonal bisphenoid of the second order;  $\{0 k l\}$  left tetragonal bisphenoid of the second order. Each 4 faces.  
 $\{h k l\}$  Left positive tetragonal bisphenoid of the third order;  $\{k h l\}$  right positive form of same;  $\{h \bar{k} l\}$  right negative form;  $\{k \bar{h} l\}$  left negative form. Each 4 faces.

The only substance which has yet been observed to crystallise in accordance with this class of symmetry is a silicate of lime and alumina,  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , which was isolated by Weyberg<sup>1</sup> in the year 1906. Both varieties of bisphenoids were observed, although rarely on the same crystal, together with the forms  $\{001\}$  and  $\{110\}$ . The etch-figures on the faces of the two latter forms (basal pinakoid and first order prism), afforded by hydrochloric and nitric acids, exhibited clear evidence of bisphenoidal symmetry.

*Class 9.—Pyramidal Class. Hemimorphic-Hemihedral Class.*  
*Type, Pyramidal Polar.*

This final class of lowest possible tetragonal symmetry is distinguished by the possession of only one element of symmetry, the indispensable tetragonal axis persistent throughout the system, and which is in this class polar.

As will be evident from the stereographic projection Fig. 171, which exhibits both the symmetry element and the poles of the general form  $\{hkl\}$ , repetition of the face

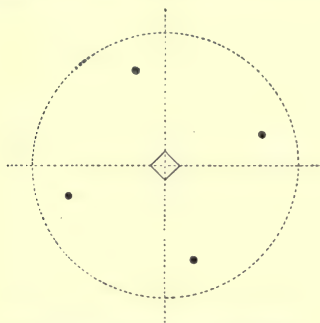


FIG. 171.—Symmetry Element and General Form of Class 9.

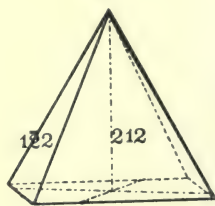


FIG. 172.  
The Tetragonal Pyramid.

( $hkl$ ) about the tetragonal axis results in the production of an open simple equi-four-faced pyramid, the **tetragonal pyramid**, shown in Fig. 172. It may be closed by a single basal plane, for the basal pinakoid in this class falls into two separate forms,  $\{001\}$  and  $\{00\bar{1}\}$ . It is obvious also that to the four-faced upper pyramid  $\{hkl\}$  there corresponds a duplicate lower pyramid  $\{h\bar{k}l\}$ . Moreover, just as in the bipyramidal

<sup>1</sup> *Anzeiger der Akad. der Wiss., Krakau, 1906, 611.*

class 12, in which these two forms together make up one form, there are two other complementary forms (together also making up one form in the bipyramidal class) having the same numbers in their indices, and which have therefore the same interfacial angle, namely, the form  $\{khl\}$  of four faces and the corresponding lower form  $\{k\bar{h}\bar{l}\}$ . Hence, there are in all four forms of the general type  $\{hkl\}$  in this class. They are all pyramids of the third order, indistinguishable except by their positions *in situ*. This is not, however, a case of true tetartohedrism, but merely of hemihedrism having a hemimorphic character. The truly tetartohedral forms belong to class 10 of the tetragonal system.

When  $h=k$  and the poles fall consequently on the  $45^\circ$ -diameters, we have an open pyramid of the first order produced, which may be closed by the basal plane. When  $l$  is negative, we have the corresponding lower pyramid.

When either  $h$  or  $k$  is 0, on the other hand, the poles migrate to the crystallographic axial diameters, and we then have the upper and lower pyramids of the second order produced, which also may be closed by the basal plane.

If  $l=0$ , and the poles migrate consequently on to the primitive circle, the prisms of the first, second, or third orders are formed, of the third of which there are two varieties,  $\{hk0\}$  and  $\{k00\}$ . All these separate varieties of each of the various pyramids and prisms are indistinguishable from each other, except when in their positions of derivation from the holohedral form.

Finally, if the poles approach the centre, the pyramids become flatter and flatter, until when the poles coincide in the centre the upper pyramids yield the basal plane  $\{001\}$  and the lower pyramids the second face, now a separate form, of the basal pinakoid  $\{00\bar{1}\}$ .

There are thus to be distinguished the following forms in the class :

*List of Forms in Class 9.*

- $\{001\}$  Upper positive basal plane or pedion ;  $\{00\bar{1}\}$  lower negative basal plane or pedion. Each 1 face.  
 $\{110\}$  Tetragonal prism of the first order. 4 faces.  
 $\{100\}$  Tetragonal prism of the second order. 4 faces.  
 $\{hk0\}$  Tetragonal right-hand prism of the third order ;  $\{kh0\}$  tetragonal left-hand prism of the third order. Two solids indistinguishable. Each 4 faces.  
 $\{hhl\}$  Upper tetragonal pyramid of the first order ;  $\{hh\bar{l}\}$  lower tetragonal pyramid of the first order. Two solids indistinguishable. Each 4 faces.  
 $\{h0l\}$  Upper tetragonal pyramid of the second order ;  $\{h0\bar{l}\}$  lower tetragonal pyramid of the second order. Two solids indistinguishable. Each 4 faces.  
 $\{hkl\}$  Upper right tetragonal pyramid of the third order ;  $\{khl\}$  upper left form ;  $\{hk\bar{l}\}$  lower right form ;  $\{kh\bar{l}\}$  lower left form. Four solids indistinguishable. Each 4 faces.
- 
- The diagram shows a tetragonal pyramid with a square base and four triangular faces. The front-left face is labeled '111' and the front-right face is labeled '111-bar' (represented as 111 with a bar over the last digit). Dashed lines indicate the hidden edges of the pyramid.

Wulfenite, the natural molybdate of lead,  $\text{PbMoO}_4$ , forms an excellent example of a substance crystallising according to this class of symmetry. Fig. 173 shows a crystal of wulfenite exhibiting a combination of the five pyramids  $\{111\}$ ,  $\{10\bar{1}\}$ ,  $\{11\bar{1}\}$ ,  $\{31\bar{1}\}$ , and  $\{432\}$ . The axial ratio is  $a : c = 1 : 1.5777$ .

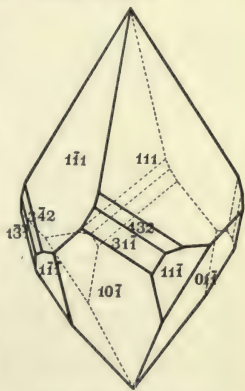


FIG. 173.—Wulfenite.



## CHAPTER XIII

### PRACTICAL EXAMPLE OF A TETRAGONAL CRYSTAL

#### *Class 15.—Tetragonal Holohedral. Anatase, $TiO_2$ .*

THE crystal of anatase which forms our example is a beautifully developed specimen about two millimetres in average diameter, and very rich in faces, no less than forty-eight being developed. Its appearance is shown in Fig. 174, drawn to scale with the aid of the usual preliminary careful freehand drawing, after the completion of the calculations, by the ordinary

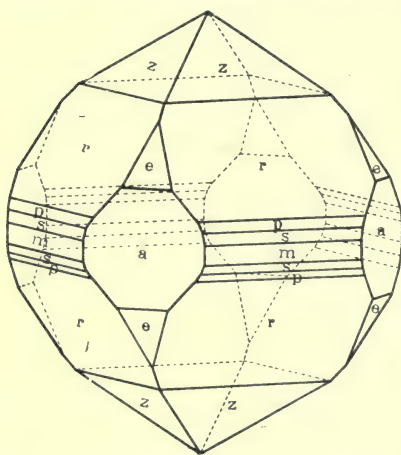


FIG. 174.  
The Crystal of Anatase used as Example.

conventional method described in Chapter XXV., where the construction will be given in detail. Its stereographic projection is given in Fig. 175, and the process of constructing it will be described stage by stage.

The crystal was brownish-yellow in colour, more or less transparent (translucent), and the faces were exceedingly brilliant, exhibiting the well-known adamantine lustre of anatase.

The exterior shape of the crystal, on the average more or less spherical, was chiefly determined by three forms, which will be shown in the sequel to be the tetragonal prism of the second order  $a=\{100\}$ ,

the tetragonal bipyramid of the first order  $z=\{113\}$ , and the bipyramid also of the first order  $r=\{335\}$ . The only other form observable at first sight on the crystal is one of smaller faces, symmetrically replacing the eight solid angles formed by the intersection of the forms  $a$  and  $r$ ; it is the tetragonal primary bipyramid of the second order  $e=\{101\}$ . Here and there, however, the equatorial edges of intersection of the faces of the form  $r=\{335\}$  showed reflections as if from other narrow faces, and as a matter of fact the faces of three other forms were present, which will be shown to be two further bipyramids of the first order,  $p=\{111\}$  the

parametral form, and  $s = \{221\}$ ; and the tetragonal prism of the first order  $m = \{110\}$ . The parametral form is not prominent on this crystal, although it often is so on crystals of anatase from particular localities; notwithstanding this fact, the mode of description of the crystal will be that currently accepted, according to which  $p$  is the parametral form  $\{111\}$ .

On making a careful study of the crystal with the eye and pocket lens, turning it round and round on the little wax cone of the crystal-holder, two prominent features were observed indicative of a promising mode of commencing the measurements. Firstly, there was clearly a zone of four tolerably large and well-developed faces arranged at what appeared to be a right angle to each other. Secondly, there were two mutually similar zones of large faces, crossing each other rectangularly, which appeared to intersect in two sharply pointed four-faced pyramidal terminations, one above the zone plane of the rectangular zone and one below, the points being apparently the ends of the vertical axis running parallel to

the four faces just referred to meeting in right angles. The zone planes of these two pyramidal zones appeared to bisect the angles between adjacent rectangular faces, as if they were composed of first-order pyramid faces with poles on diameters of a tetragonal projection arranged at  $45^\circ$  to the axial diameters, assuming the latter to be the normals of the four rectangularly inclined faces. There were four pairs of these large pyramidal faces in each of the two zones, each pair consisting of closely adjacent faces belonging to two pyramids of different altitudes and occupying one octant, so that there were eight of these pairs altogether, apparently symmetrically arranged in the eight octants.

Our obvious first duty was to measure the apparently rectangular zone. For this purpose the crystal was set up on the wax cone by one of the pointed pyramidal ends, the line joining the two such ends being vertical, as in Fig. 174. The four apparently rectangular faces were first adjusted and centred, and then definitely found to belong to the same zone, and four other very narrow but elongated faces were found to alternate with them in the zone at apparently equal distances between each pair of

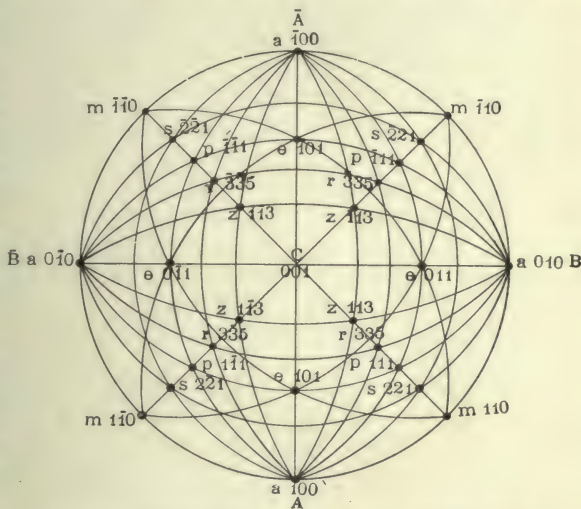


FIG. 175.—Stereographic Projection of the Anatase Crystal.

them; only two of these narrow faces gave good reflections, the other two being mere lines. Proceeding then to measure the zone, the following readings were obtained:

## TETRAGONAL PRISM ZONE.

Circle Reading.	Angle.
$\left\{ \begin{array}{l} a \ 359^\circ \ 56' A \\ a \ 269 \ 56 \ A \\ m \ 224 \ 56 \ A \\ a \ 179 \ 56 \\ m \ 134 \ 55 \ A \\ a \ 89 \ 55 \ A \\ a \ 359 \ 56 \ A \end{array} \right.$	$\left\{ \begin{array}{l} aa \ 90^\circ \ 0' A \\ am \ 45 \ 0 \ A \\ ma \ 45 \ 0 \\ am \ 45 \ 1 \\ ma \ 45 \ 0 \ A \\ aa \ 89 \ 59 \ A \end{array} \right. \begin{array}{l} aa \ 90^\circ \ 0' \\ aa \ 90^\circ \ 0' \\ aa \ 90 \ 1 \end{array}$

It will be clear from these measurements that the four prominent faces of the zone, those marked with the letter *a*, were truly at right angles to each other, that is, composed of two pairs of parallel faces the planes of which were exactly at  $90^\circ$  to each other. Moreover, the intermediate faces marked *m* were situated exactly  $45^\circ$  from them, so that we are justified in assuming that in all probability the zone is either one of a cubic crystal, or is the prism zone of a tetragonal crystal. The whole of the measured values of the angles are exactly either  $90^\circ \ 0'$  or  $45^\circ \ 0'$  or within  $1'$  of these round values, hence there can be no question as to nature's evident intention to erect these faces exactly at  $90^\circ \ 0'$  and  $45^\circ \ 0'$  to each other.

We may next with greatest advantage measure the two zones each of which is apparently formed by a pair of parallel *a*-faces and four of the eight small faces marked *e*, which have been referred to on the first page of this chapter as replacing the solid angles formed by the intersection of the large faces *a* and *r*. From the situation of these little *e*-planes it appeared probable that they were faces of either the cubic rhombic dodecahedron (in which case the angle *ae* would be  $45^\circ$ ) or its tetragonal equivalent, a tetragonal pyramid of the second order.

In order to measure these two zones, the crystal was set in each case on the wax cone by one of the *a*-faces belonging to the complementary zone, that is with this *a*-face horizontal. On adjusting the pair of *a*-faces (perpendicular to this) of the zone to be measured truly vertical and parallel to one of the two adjusting movements, and adjusting one of the small *e*-faces also by the tangent screw of this movement (afterwards completing the adjustment of the *a*-face with the other tangent screw), all four small *e*-faces in question were found, as expected, to belong to the zone, the three other than the one adjusted being also automatically adjusted. The two zones gave the following measurements:

## PAIR OF SECOND-ORDER PYRAMID ZONES.

Circle Reading.	Angle.	Circle Reading.	Angle.
$\left\{ \begin{array}{l} a \ 360^\circ \ 0' A \\ e \ 330 \ 35 \\ e \ 209 \ 19 \\ a \ 180 \ 3 \\ e \ 150 \ 35 \\ e \ 29 \ 23 \ A \\ a \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} ae \ 29^\circ \ 25' \\ ee \ 121 \ 16 \\ ea \ 29 \ 16 \\ ae \ 29 \ 28 \\ ee \ 121 \ 12 \\ ea \ 29 \ 23 \ A \end{array} \right.$	$\left\{ \begin{array}{l} a \ 360^\circ \ 0' A \\ e \ 330 \ 39 \ A \\ e \ 209 \ 23 \ A \\ a \ 180 \ 5 \ A \\ e \ 150 \ 45 \ A \\ e \ 29 \ 29 \\ a \ 0 \ 4 \ A \end{array} \right.$	$\left\{ \begin{array}{l} ae \ 29^\circ \ 21' A \\ ee \ 121 \ 16 \ A \\ ea \ 29 \ 18 \ A \\ ae \ 29 \ 20 \ A \\ ee \ 121 \ 16 \\ ea \ 29 \ 25 \end{array} \right.$



An examination of these values at once renders it clear that the two zones are similar, that there are only two different angles, symmetrically situated in the zone, and that the angle  $ae$  is not  $45^\circ$  but somewhere near  $29\frac{1}{2}^\circ$ , so that the form  $e$  is not the rhombic dodecahedron but in all probability a tetragonal bipyramid of the second order. The proof that the angles  $ae$  and  $ea$  are all intended to be identical in magnitude is afforded by the "A" values, which are sufficiently close to indicate that the angle  $ea$  on one side of any face  $a$  is of equal value with the angle  $ae$  on the other side of the face  $a$ ; and, moreover, that this pair of angles have the same magnitude and same value as regards the symmetry as the pair on the two sides of the parallel  $a$ -face. Further, the two pairs of such angles on the two zones are undoubtedly intended to be both of identical magnitude and of equal symmetric value. Having decided this, entirely from the consideration of the individual angular values of the two zones, **and not before**, we may adopt the best method open to us of ascertaining the true magnitude of the angle, by taking the arithmetical mean of all the trustworthy values, which in this case include all the values. The mean value thus obtained for  $ae$  and  $ea$  is  $29^\circ 22'$ , and for the larger angle  $ee$   $121^\circ 15'$ .

Very emphatic caution must again be given as to the taking of mean values of such series of angles. It must never be done without having first, as we have done here, absolutely decided that the angles the mean of which is being taken are of equal symmetric value, as in the case just dealt with, from a consideration of the most trustworthy individual "A" measurements; and this symmetry must be confirmed by the results of the measurement of other zones on the crystal, as will be shown to be true in this case of anatase. Otherwise a grave mistake may be made, and a higher type of symmetry assumed than is actually developed. For there are many cases known in which the actual angles are a few minutes only removed from those which would correspond to a higher system of symmetry. For instance, the prism zone of rhombic potassium sulphate has been shown in Chapter IV. to be only  $12'$  removed from  $60^\circ$ , the angle of a hexagonal prism. This pitfall is most alluring, and fatal if fallen into, and too strong a warning cannot be given with regard to it. When, however, the extraction of the mean value has been decided to be truly legitimate, it affords the best mode of eliminating the fortuitous slight variations of a **very** few minutes due to disturbance of the conditions during growth.

We proceed next to the measurement of the pair of apparently first-order pyramid zones, the two very prominent zones of large faces crossing each other apparently rectangularly and at  $45^\circ$  to the vertical axial-plane zones already measured. On adjusting each of these two zones in turn, it was found that besides the large faces lettered  $z$  and  $r$ , and the smaller faces of the first-order prism  $m$ , there were also automatically adjusted small faces of two other forms, lettered  $p$  and  $s$ . They were generally only narrow strips, but one  $p$ -face was quite well developed and gave an excellent reflection. This form lettered  $p$  will be shown in the sequel

to be the important parametral form  $\{111\}$ . The actual results of the measurements are given below :

PAIR OF FIRST-ORDER PYRAMID ZONES.

Circle Reading.	Angle.	Circle Reading.	Angle.
<i>m</i> 360° 0'A <i>p</i> 338 22 A <i>r</i> 326 29 A <i>z</i> 309 55 A <i>z</i> 230 3 A <i>r</i> 213 30 A <i>m</i> 180 0 <i>r</i> 146 28 <i>z</i> 129 57 A <i>z</i> 50 3 A <i>r</i> 33 31 A <i>p</i> 21 42 <i>s</i> 11 15 A <i>m</i> 0 0 A	<i>mp</i> 21° 38'A <i>pr</i> 11 53 A <i>mr</i> 33° 31'A <i>rz</i> 16 34 A <i>mz</i> 50 5 A <i>zz</i> 79 52 A <i>zr</i> 16 33 A <i>zm</i> 50 3 <i>rm</i> 33 30 <i>mr</i> 33 32 <i>mz</i> 50 3 A <i>rz</i> 16 31 <i>zz</i> 79 54 A <i>zr</i> 16 32 A <i>zm</i> 50 3 A <i>rp</i> 11 49 <i>rm</i> 33 31 A <i>ps</i> 10 27 <i>pm</i> 21 42 <i>sm</i> 11 15 A	<i>z</i> 360° 0'A <i>z</i> 280 7 A <i>r</i> 263 38 A <i>p</i> 251 40 A <i>s</i> 241 14 A <i>m</i> 230 4 A <i>s</i> 218 46 A <i>p</i> 208 26 <i>r</i> 196 30 A <i>z</i> 180 0 A <i>z</i> 100 7 A <i>r</i> 83 36 A <i>p</i> 71 48 <i>p</i> 28 21 A <i>r</i> 16 31 A <i>z</i> 0 0 A	<i>zz</i> 79° 53'A <i>zr</i> 16 29 A <i>zm</i> 50° 3'A <i>rp</i> 11 58 <i>rm</i> 33 34 A <i>ps</i> 10 26 <i>pm</i> 21 36 <i>sm</i> 11 10 A <i>ms</i> 11 18 A <i>sp</i> 10 20 <i>mp</i> 21 38 <i>pr</i> 11 56 <i>mr</i> 33 34 A <i>rz</i> 16 30 A <i>mz</i> 50 4 A <i>zz</i> 79 53 A <i>zr</i> 16 31 A <i>rp</i> 11 48 <i>pp</i> 43 27 <i>pr</i> 11 50 A <i>rz</i> 16 31 A

Similar angles in these two zones so rich in faces are collected together in the following lists, a slight gap being left in each table to indicate where the values from the second zone begin ; and the mean value is given below the line :

<i>zz.</i>	<i>zr.</i>	<i>rp.</i>	<i>ps.</i>	<i>sm.</i>	<i>pm.</i>	<i>rm.</i>	<i>zm.</i>
79° 52'A	16° 34'A	11° 53'A	10° 27'	11° 15'A	21° 38'A	33° 31'A	50° 5'A
79 54 A	16 33 A	11 49			21 42	33 30	50 3
	16 31		10 26	11 10 A		33 32	50 3
79 53 A	16 32 A	11 58	10 20	11 18 A	21 36	33 31 A	50 3 A
79 53 A		11 56			21 38		
	16 29 A	11 48	10° 24'	11° 14'		33 34 A	50 3 A
79° 53'	16 30 A	11 50 A			21° 39'	33 34 A	50 4 A
	16 31 A						
	16 31 A	11° 52'				33° 32'	50° 4'
	16° 31'						

It will be clear that, firstly, the two zones are exactly similar and equiangular, and secondly, that in each zone the pyramidal poles *s*, *p*, *r*, and *z* are repeated in the same order and at the same angles four times in the zone, symmetrically placed as regards the prism poles *m*. Take, for instance, the four values of the angle *zz*, two in each zone ; there can be no question but that these four angles were intended by nature to be equal, for the two values in one zone were absolutely equal, and in the other zone only two minutes different, 1' on each side of the mean value of the four. Hence we are fully justified in accepting the mean value as the true angle. The measurements obviously indicate that *z*, *r*, *p*, and *s* are a series of four tetragonal bipyramids in ascending order of steepness,

$m$  being the limiting case of the prism itself, with faces perfectly vertical.

We are now in a position to construct the stereographic projection, Fig. 175 on page 209.

Commencing with the primitive circle, we mark off along it the positions of the four  $a$ -poles at the rectangular positions and the four  $m$ -poles at the intermediate  $45^\circ$ -positions, and then join opposite poles by diameters. Dots are to be placed at the ends of all the diameters on the primitive circle, in order to mark the positions of the poles  $a$  and  $m$ . On the diameters parallel to the page edges, the crystallographic axial diameters, we are next to find the positions of the four poles of the second-order bipyramid  $e$ . The angle  $ae$  has been shown to be  $29^\circ 22'$ . Suppose we find the position of the  $e$ -pole on the front radius  $ac$ , which not only represents the axis  $a$  but also the quadrant-arc (of a great circle)  $ca = (001) : (100)$ . The two poles of this zone-circle are clearly  $a = (010)$  and  $a = (0\bar{1}0)$ . In accordance with the instructions fully given in Chapter VI., we mark off along the primitive circle from  $a = (100)$  an angle  $29^\circ 22'$  with the protractor, on either side of  $a = (100)$ . We then join this point so marked off to the opposite pole of the zone-circle, that is, to that one of its two poles just mentioned which lies on the other side to that on which the point was just now marked off; if we marked off to the right, we join that point to  $a = (0\bar{1}0)$ . This joining line will then pass through the position of the required pole  $e$  on the radius  $c = (001) : a = (100)$ . Having thus found one pole  $e$ , we mark off on the other three rectangular radii similar points  $e$  at the same distance from the centre, when we shall thus have found the positions of all four  $e$ -poles on the projection. We next proceed to find the positions of the first-order bipyramid poles  $z$ ,  $r$ ,  $p$ , and  $s$ . It will be sufficient to find their positions on one diagonal radius, and then to transfer the same distances on to the other 3 radii, from the centre  $c$  (actually marked with the axial letter  $C$  in Fig. 175, no  $c$ -face being developed), in order to get the others. The angles  $ms$ ,  $mp$ ,  $mr$ , and  $mz$  have been shown to be respectively  $11^\circ 14'$ ,  $21^\circ 39'$ ,  $33^\circ 32'$ , and  $50^\circ 4'$ ; we mark off, therefore, from  $m$  along the primitive circle on one side, these successive angular arcs, and then join the points thus marked off to that pole of the zone circle which lies on the other side. Suppose, for instance, we are going to find the positions on the radius  $c = (001) : m = (110)$ ; the poles of the zone circle of which this radius is the semi-projection are at the extremity of the perpendicular diameter, on the primitive circle, namely,  $m = (\bar{1}10)$  and  $m = (1\bar{1}0)$ , and if we mark off the angles  $ms$ ,  $mp$ ,  $mr$ , and  $mz$  to the right from  $m = (110)$  we must join the marked points on the primitive circle to  $m = (\bar{1}10)$ . The points where these junction lines intersect the radius  $c = (001) : m = (110)$  are the required positions of the facial poles  $s$ ,  $p$ ,  $r$ , and  $z$ . From the centre  $c$  we then mark off along the other three diagonal radii the distances  $cz$ ,  $cr$ ,  $cp$ , and  $cs$ , in order to find the positions of the other facial poles of the same bipyramidal forms  $z$ ,  $r$ ,  $p$ , and  $s$ .

We may next connect each adjacent pair of  $z$ -poles,  $r$ -poles,  $p$ -poles, and  $s$ -poles with the  $a$ -poles lying in the same zone with them, by a circular arc to represent the zone as shown in Fig. 175. The method of finding the centre for each is, stated generally, that of the simple problem in plane geometry "to construct a circular arc to pass through three given points," the three points being any three of the four poles  $azza$ , or of  $arra$ , or of  $appa$ , or of  $assa$ ; bisecting perpendiculars are drawn to the two imaginary straight lines joining the first and second points, and the second and third points, and where the two perpendiculars intersect is the required centre. This centre, however, must lie on that axial diameter perpendicular to the one which joins the ends  $aa$  of the zone-arc in question, so that it is only necessary to draw one of the bisecting perpendiculars, and where it cuts the axial diameter is the centre required. We shall then find that there are 16 such secondary zones altogether, composed of four sets of four equal zones.



This indicates the next step to be taken in the measurements, namely, that each of these four different types of zones should be measured, and at least two of the four similar ones of each type, in order to confirm still more fully the tetragonal nature of the symmetry; and the pair of each measured should not always be the analogous pair, but should be so selected as to get confirmations of the tetragonal arrangement all round the circle, so that the evidence shall be as strong as if all the 16 zones had been measured instead of only eight of them.

Commencing at the apex of the pyramid, we measure first a couple of the zones [azza]. The actual readings and angles are as under:

TWO OF THE FOUR ZONES [azza].

Circle Reading.	Angle.	Circle Reading.	Angle.
$\left\{ \begin{array}{l} z \ 360^\circ \ 0'A \\ z \ 306 \ 0 \ A \\ a \ 242 \ 59 \ A \\ z \ 180 \ 1 \ A \\ z \ 126 \ 1 \ A \\ a \ 63 \ 4 \ A \\ z \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} zz \ 54^\circ \ 0'A \\ za \ 63 \ 1 \ A \\ az \ 62 \ 58 \ A \\ zz \ 54 \ 0 \ A \\ za \ 62 \ 57 \ A \\ az \ 63 \ 4 \ A \end{array} \right.$	$\left\{ \begin{array}{l} z \ 360^\circ \ 0'A \\ a \ 297 \ 3 \ A \\ z \ 233 \ 59 \ A \\ z \ 180 \ 0 \ A \\ a \ 116 \ 58 \ A \\ z \ 54 \ 1 \ A \\ z \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} za \ 62^\circ \ 57'A \\ az \ 63 \ 4 \ A \\ zz \ 53 \ 59 \ A \\ za \ 63 \ 2 \ A \\ az \ 62 \ 57 \ A \\ zz \ 54 \ 1 \ A \end{array} \right.$

It is obvious that there are only two different angles, of about  $54^\circ$  and  $63^\circ$  respectively, and a study of the two lists of similar angles shows clearly that this is again a case where we are justified in taking the two mean values, which are  $54^\circ \ 0'$  and  $63^\circ \ 0'$ . In the case of  $zz$ , which was measurable with the greater accuracy owing to the higher excellence of the images from the  $z$ -faces, the identity is within  $2'$  of being absolute, and in the case of the angle  $az$ , the slight variations of  $3'$  or  $4'$  each side of the mean is only owing to the lesser excellence of the images from the  $a$ -faces when adjusted for these oblique zones. The two particular zones measured were the intersecting ones [ $a=(100):z=(113):z=(\bar{1}13)$ ] and [ $a=(010):z=(113):z=(1\bar{1}3)$ ], so that we have here further confirmation of the tetragonal nature of the symmetry.

Passing next to the zones [arra], the following measurements were obtained with a pair of them, the particular pair being [ $a=(100):r=(335):r=(\bar{3}35)$ ] and [ $a=(010):r=(\bar{3}35):r=(335)$ ], so that this pair of zones will afford complementary evidence to the last pair:

TWO OF THE FOUR ZONES [arra].

Circle Reading.	Angle.	Circle Reading.	Angle.
$\left\{ \begin{array}{l} r \ 360^\circ \ 0'A \\ r \ 287 \ 44 \ A \\ a \ 233 \ 52 \ A \\ r \ 179 \ 56 \ A \\ r \ 107 \ 44 \\ a \ 53 \ 50 \\ r \ 0 \ 1 \ A \end{array} \right.$	$\left\{ \begin{array}{l} rr \ 72^\circ \ 16'A \\ ra \ 53 \ 52 \ A \\ ar \ 53 \ 56 \ A \\ rr \ 72 \ 12 \\ ra \ 53 \ 54 \\ ar \ 53 \ 49 \end{array} \right.$	$\left\{ \begin{array}{l} r \ 360^\circ \ 0'A \\ r \ 287 \ 42 \ A \\ a \ 233 \ 50 \ A \\ r \ 179 \ 58 \ A \\ r \ 107 \ 44 \\ a \ 53 \ 48 \\ r \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} rr \ 72^\circ \ 18'A \\ ra \ 53 \ 52 \ A \\ ar \ 53 \ 52 \ A \\ rr \ 72 \ 14 \\ ra \ 53 \ 56 \\ ar \ 53 \ 48 \end{array} \right.$

As in the case of the previous zone [azza], it is clear that there are only two different angles, symmetrically distributed about the  $a$ -poles, and the mean value extracted from the two lists of their individual values are  $rr=72^{\circ} 15'$  and  $ar=53^{\circ} 52'$ .

Tetragonal symmetry is again borne out by the individual values, especially the "A" values; thus these values for  $rr$  from the two zones only differ by  $2'$ , and three out of four "A" values for  $ar$  from both zones are absolutely identical.

We pass next to the important parametral zone [appa], which is of the same character, except that most of the  $p$ -readings are derived from very small faces, there having been only one good-sized  $p$ -face developed on the crystal, and also that each of these four similar zones also includes two  $e$ -faces, each situated half-way between two  $p$ -faces. The measurements derived from a pair of these zones are as under, the actual pair chosen having been those containing the best  $p$ -faces:

TWO OF THE FOUR PARAMETRAL ZONES [appa].

Circle Reading.	Angle.	Circle Reading.	Angle.
$e$ 360° 0'A	$ep$ 41° 5'A	$a$ 360° 0'A	$ap$ 48° 54'A
$p$ 318 55 A	$pa$ 48 59	$p$ 311 6 A	$pe$ 41 0
$a$ 269 56	$ap$ 48 47	$e$ 270 6	$ep$ 41 8 $pp$ 82° 8'A
$p$ 221 9	$pe$ 41 7	$p$ 228 58 A	$pa$ 48 55 A
$e$ 180 2	$ep$ 41 8 $pp$ 82° 15'	$a$ 180 3 A	$ap$ 48 57
$p$ 138 54	$pa$ 48 58	$p$ 131 6	$pe$ 41 7
$a$ 89 56	$ap$ 48 50	$e$ 89 59	$ep$ 41 1 $pp$ 82 8
$p$ 41 6 A	$pe$ 41 6 A $pp$ 82 11 A	$p$ 48 58	$pa$ 48 58
$e$ 0 0 A		$a$ 0 0 A	

The "A" values of  $ap$  and of  $pe$  only differ in each case by  $1'$ , so that we may accept it as a fact that all the  $ap$  values were intended to be the same and all the  $pe$  angles to be identical. Owing to the less excellent character of some of the  $p$ -faces a few of the angles intended to be identical gave rather wider readings than in the cases of those derived from the better faces, but the divergences are not great, and we can legitimately take the mean of symmetrically analogous and equal angles, which will be found to yield the same value as the "A" values alone, namely  $ap=48^{\circ} 55'$ ,  $pe=41^{\circ} 5'$ , and  $pp=82^{\circ} 10'$ .

We next pass on to the last of these four secondary arc-zones, namely [assa]. The readings and angles for a pair of them as far as developed are as under:

TWO OF THE FOUR ZONES [assa].

Circle Reading.	Angle.	Circle Reading.	Angle.
$a$ 360° 0'	$as$ 46° 7'	$a$ 360° 0'A	$as$ 46° 1'A
$s$ 313 53	$ss$ 87 47	$s$ 313 59 A	$ss$ 87 51 A
$s$ 226 6	$sa$ 46 4	$s$ 226 8 A	$sa$ 46 8 A
$a$ 180 2 A	$as$ 46 9	$a$ 180 0 A	
$s$ 133 53	$ss$ 87 45		
$s$ 46 8	$sa$ 46 6		
$a$ 0 2			

The readings in the first zone were not quite so satisfactory as usual, on account of the small size of the *s*-faces and the somewhat poorer quality of the images reflected by them. The second zone had only two *s*-faces developed, but they gave "A" images of the signal. We have now accumulated such a mass of evidence, however, that the symmetry is tetragonal, that we may here also with confidence take the mean values as a close approximation to the truth, leaving the calculations from the irreproachable basal angles to check the values arrived at. Even as they stand, the divergence never exceeds 8'. The mean value for  $as = 46^\circ 6'$ , and for  $ss = 87^\circ 48'$ .

There is still one further set of four zones that it is desirable to measure, namely, those connecting each parallel pair of *m*-faces with four of the *e*-faces, as indicated by the four circular arcs in the projection, drawn from the ends of the diagonals *mm* to pass through the *e*-poles by the usual method of describing a circular arc to pass through three given points, as already described in the cases of the four arc-zones already completed. Two of these four equal zones [*meem*] were measured, namely, [ $m = (110), e = (101), e = (0\bar{1}1), m = (\bar{1}\bar{1}0)$ ] and [ $m = (1\bar{1}0), e = (101), e = (011), m = (\bar{1}10)$ ]. The record of the observations is as under:

TWO OF THE FOUR ZONES [*meem*].

Circle Reading.	Angle.	Circle Reading.	Angle.
$\left\{ \begin{array}{l} e \ 360^\circ \ 0'A \\ e \ 283 \ 53 \ A \\ m \ 231 \ 54 \ A \\ e \ 180 \ 0 \\ e \ 103 \ 54 \\ e \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} ee \ 76^\circ \ 7'A \\ em \ 51 \ 59 \ A \\ me \ 51 \ 54 \\ ee \ 76 \ .6 \end{array} \right.$	$\left\{ \begin{array}{l} m \ 360^\circ \ 0' \\ e \ 308 \ 3 \ A \\ e \ 231 \ 55 \\ m \ 180 \ 0 \ A \\ e \ 128 \ 2 \ A \\ e \ 51 \ 55 \ A \\ m \ 0 \ 1 \ A \end{array} \right.$	$\left\{ \begin{array}{l} me \ 51^\circ \ 57' \\ ee \ 76 \ 8 \\ em \ 51 \ 55 \\ me \ 51 \ 58 \ A \\ ee \ 76 \ 7 \ A \\ em \ 51 \ 54 \ A \end{array} \right.$

It is quite clear that all four values of *ee* belong to angles of equal value as regards the symmetry, the maximum difference among them being only 2', and the same naturally follows for *me*, although the difference amounts to 5', which, however, is still small enough to indicate nature's slightly disturbed attempt at identity. These measurements finally complete the proof that the symmetry of the crystal is tetragonal, and having now fully convinced ourselves, from the whole of the measurements, of this fact, we can with confidence accept the mean of the *me*-values, namely,  $51^\circ 56'$ , and the mean of the *ee*-values,  $76^\circ 7'$ , as representing the true magnitudes of those angles.

This completes our practical study of the crystal of anatase, and we may now address ourselves to the calculation of the elements, and of the angles other than the basal angle, for purposes of confirmation.

#### *Calculation of Elements and Angles of Anatase.*

**Basal angle,**  $ae = (100) : (101) = 29^\circ 22'$ . This angle is very convenient to choose for the one basal angle required in the tetragonal system, as it enables us immediately to calculate the axial ratio. It



was measured eight times in a fully trustworthy manner, with only  $5'$  between the extreme "A" values. Also the "A" value of the supplementary angle in the zone,  $ee=(101):\bar{1}01$ , was identical with the value  $121^\circ 16'$  which it should possess if  $ae=29^\circ 22'$ . For  $ee=180^\circ-2ae=180^\circ-58^\circ 44'=121^\circ 16'$ .

Hence we can take  $ae=29^\circ 22'$  with great confidence as the basal angle.

#### To find the axial ratio, $a:c$ .

We can calculate this fundamental constant directly from first principles. Fig. 176 represents diagrammatically the relations of the face  $e=(101)$  to the horizontal axis  $a$  and the vertical axis  $c$ . The face is inclined so that the angle between the normal to  $a=(100)$ , which is the axis  $a$ , and the normal to the face  $e=(101)$  itself, is  $29^\circ 22'$ , that is the angle  $aOe$  is  $29^\circ 22'$ . But this is also the magnitude of the angle  $acO$ , by the principle of similar triangles, and the axial ratio required is that of the two sides  $Oa$  and  $Oc$  of the right-angled triangle  $acO$  to one another, which ratio is obviously the tangent of the angle at  $c$ ,  $29^\circ 22'$ , the basal angle.

Now the ratio of the axes in the tetragonal system is always expressed in the form that  $a=1$ , and it does not matter whether we consider the front-to-back axis  $a$  or the lateral right-and-left axis also lettered  $a$ , both being equal. Consequently we shall set out our ratio from Fig. 176 in the following form, which enables us to calculate the value of  $c$  compared with  $a=1$ :

$$c:a=Oc:Oa; \text{ or } \frac{c}{a}=\frac{Oc}{Oa}=\cot 29^\circ 22'.$$

As  $a=1$  we have  $c=\cot 29^\circ 22'=1.7771$ .

Or, writing the axial ratio in the form in which it is usually presented:

$$a:c=1:1.7771.$$

This is in absolute agreement with the value of the ratio given by Dana.

The same result is equally well arrived at by the application of the general method of calculating axial ratios, given in Chapter VII., to the case of tetragonal crystals as stated on page 111 of that chapter. It is there shown, and will also be obvious from the above, that as  $a=b$  the tetragonal ratio  $c/a$  is the same as that for  $c/b$  and that:

$$\frac{c}{b}=\frac{\sin \psi}{\sin \chi}.$$

Now  $\psi$  is the angle  $ce=\frac{1}{2}ee$  (Fig. 175), and  $\chi$  is the complementary angle  $ae$ , the two making up the  $90^\circ$  axial angle  $ac$ , so that we have:

$$\frac{c}{a}=\frac{c}{b}=\frac{\sin ce}{\sin ae}=\frac{\sin 60^\circ 38'}{\sin 29^\circ 22'}=\frac{\cos 29^\circ 22'}{\sin 29^\circ 22'}=\cot 29^\circ 22'=1.7771.$$

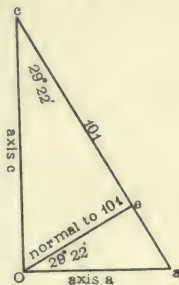


FIG. 176.

*Calculation of Interfacial Angles.*

To find the position of  $p=(111)$ , the parametral face, that is, to find  $cp=(001):(111)$ . (For stereographic projection see Fig. 175.)

We make use of the triangle  $cep=(001):(101):(111)$ , in which the angle at  $e$  is a right angle, the angle at  $c$  is  $45^\circ$ , and the side-arc  $ce$  is  $60^\circ 38'$ , the complement of the basal angle. From the Napierian diagram for this triangle, constructed as described in Chapter VII. (see Fig. 53) by Napier's rules, we obtain :

$$\cos 45^\circ = \tan 60^\circ 38' \cot ep,$$

$$\text{or :} \quad \cot ep = \cos 45^\circ \cot 60^\circ 38'. \quad ep = 68^\circ 18'.$$

$$\text{Then :} \quad pm=(111):(110)=90^\circ - 68^\circ 18' = 21^\circ 42'.$$

From the same triangle we can find  $ep=(101):(111)$ , the diagram at once affording :

$$\sin ep = \sin 45^\circ \sin 68^\circ 18'. \quad ep = 41^\circ 43'.$$

$$\text{Then :} \quad pp=(111):(\bar{1}\bar{1}1)=2 \quad ep = 82^\circ 9',$$

$$\text{and :} \quad ap = 90^\circ - 41^\circ 4' = 48^\circ 56'.$$

The measured angular values of  $pm$ ,  $ep$ ,  $pp$ , and  $ap$  were respectively  $21^\circ 39'$ ,  $41^\circ 5'$ ,  $82^\circ 10'$ , and  $48^\circ 55'$ , in all but the first case only  $1'$  removed from the calculated value, and in the case of  $pm$  only  $3'$  removed. The angle  $cp$  was not measured on account of the absence of the faces of the basal pinakoid.

To find the position of  $z=(113)$ , that is, to find  $cz=(001):(113)$ .

It was surmised that the form  $z$  was  $\{113\}$ , and confirmed by a preliminary use of the anharmonic ratio of four poles in a zone, the  $90^\circ$ -zone [ $c=(001)$ ,  $z=(113)$ ,  $p=(111)$ ,  $m=(110)$ ], taking the measured angles as correct and setting down the indices of  $z$  as  $(hhl)$ , for  $h$  worked out to be 1 and  $l$  to be 3. We are now to find the value of the angle  $cz$  by the converse process, taking the indices of  $z$  to be  $(113)$ . From the conditions in the zone-quadrant we derive the following anharmonic ratio :

$$\begin{array}{c} \begin{array}{ccccc} & 0 & 0 & 1 & 1 & 1 & 0 \\ & & & \times & & \times & \\ \frac{\sin cz}{\sin 68^\circ 18'} \cdot \frac{\sin 21^\circ 42'}{\sin mz} = & \frac{1}{0} & \frac{1}{0} & \frac{1}{1} & \frac{1}{1} & \frac{1}{1} & \frac{0}{0} \end{array} \\ \begin{array}{ccccc} & & & \times & & \times & \\ & 1 & 1 & 1 & 1 & 1 & 3 \\ \frac{\sin cz}{\sin 68^\circ 18'} \cdot \frac{\cos 68^\circ 18'}{\cos cz} = & \frac{1}{1} & \frac{1}{1} & \frac{1}{3} & \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{array} \\ \tan cz = 1/3 \tan 68^\circ 18'. \quad cz = 39^\circ 57'. \end{array}$$

This angle could not be measured because of the absence of  $c$ -faces. Its double,  $zz=(113):(\bar{1}\bar{1}3)$ , was measured, however, and found to be  $79^\circ 53'$ , the calculated value being  $79^\circ 54'$ . Also its complement,  $zm=(113):(110)$ , was measured and found to be  $50^\circ 4'$ , only  $1'$  again removed, for :

$$zm = 90^\circ - 39^\circ 57' = 50^\circ 3'.$$

To find the position of  $r=(335)$ , that is, to find  $cr=(001):(335)$ .

The indices of the form  $r$  were not so easy to surmise as those of  $z$ , for this particular form is not so common on anatase, and we are quite unassisted by any possible cross-multiplication of the zones intersecting in any  $r$ -pole, there being only one such zone,  $[crpm]$ , with more than one other known pole situated on it, two being of course required in order to be able to find the indices of the zone for use in cross-multiplication. We have, therefore, to rely entirely on the anharmonic ratio of four poles, including the as yet unknown  $r$ , in the zone  $[crpm]$ . We can either assume

some likely simple indices for  $r$  and see if the calculated angles then agree with the measured, or we can set the indices of  $r$  down in the ratio as  $(hhl)$  and assume the measured angles to be correct, and thus find  $h$  and  $l$ . The former course was first tried, as if successful at once it was the easier, assuming the indices of  $r$  to be  $(112)$ , for we knew they should be intermediate between those of  $z$  and of  $p$ ; if correct, we should have an expression for the anharmonic ratio of the following final form, analogous exactly to that for  $cz$  just calculated :

$$\tan cr = 1/2 \tan 68^\circ 18'.$$

This, however, yielded the value for  $cr$  of  $51^\circ 29'$ , whereas half the measured angle  $rr$  ( $c$  not being developed) was  $56^\circ 28'$ . Obviously, therefore, the indices of  $r$  were not  $(112)$ . The indices  $(223)$  were then tried, corresponding to the anharmonic ratio :

$$\tan cr = 2/3 \tan 68^\circ 18'.$$

This yielded  $59^\circ 10'$  for  $cr$ , so here again the correct indices had not been arrived at.

The latter of the two courses above referred to was then proceeded with, as it was desirable to find the indices now at once by an infallible method. Setting, therefore,  $r$  down as  $(hhl)$ , we have the conditions shown in Fig. 177, from which we derive the anharmonic ratio :

$$\frac{\sin 39^\circ 57'}{\cos 33^\circ 32'} \cdot \frac{\sin 33^\circ 32'}{\cos 39^\circ 57'} = \frac{001}{001} \cdot \frac{110}{110} \cdot \frac{hhl}{hhl}$$

$$\tan 39^\circ 57' \tan 33^\circ 32' = \frac{l}{h} \cdot \frac{l}{3} = \frac{l}{3h}; \text{ or } \frac{l}{h} = 3 \tan 39^\circ 57' \tan 33^\circ 32'.$$

$$\frac{l}{h} = 1.6656 = \frac{5}{3} \text{ exactly.}$$

Thus  $h=3$  and  $l=5$ , and the indices are therefore  $(335)$ .

Employing now the true indices  $(335)$ , we can calculate with confidence the angle  $cr$  from the equation analogous to that for  $cz$ , namely,

$$\tan cr = 3/5 \tan 68^\circ 18'. \quad cr = 56^\circ 27'.$$

Then also :

$$rm = 90^\circ - cr = 90^\circ - 56^\circ 27' = 33^\circ 33'.$$

This is only  $1'$  removed from the measured value of  $rm$ ,  $33^\circ 32'$ . The complementary angle  $cr$  itself was not measurable on account of the absence of the  $c$ -faces, but  $rr$  its double was measured, and the half of this  $\frac{rr}{2} = 56^\circ 28'$ .

Also it follows that :  $pr = cp - cr = 68^\circ 18' - 56^\circ 27' = 11^\circ 51'$  ; and that :  $zr = cr - cz = 56^\circ 27' - 39^\circ 57' = 16^\circ 30'$ .

The mean measured values of  $pr$  and  $zr$  were  $11^\circ 52'$  and  $16^\circ 31'$ , in each case only  $1'$  removed from the calculated value.

In a precisely similar manner a preliminary use of the anharmonic ratio of the four poles  $[cp sm]$ , assuming the correctness of the measured angles involving  $ms$  and  $sp$  and setting down the indices of  $s$  as  $(hhl)$ , indicated that the latter were  $(221)$ , for  $h$  came out to be 2 and  $l$  to be 1. We now use these indices to find the position of  $s$  by means of the same anharmonic ratio in which the angles involving the other three poles are such as have been already calculated and are thus known with certainty.

To find  $ms = (110) : (221)$  and  $sp = (221) : (111)$ .

From the conditions in the quadrant of the zone the anharmonic ratio is as follows :

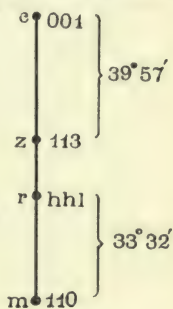


FIG. 177.



$$\begin{array}{rcc}
 & 110 & 001 \\
 & \times & \times \\
 \frac{\sin ms}{\cos cp} \cdot \frac{\sin cp}{\cos ms} = & \frac{221}{110} \cdot \frac{111}{001}, \\
 & \times & \times \\
 & 111 & 221 \\
 \tan ms \tan cp = & \frac{1}{1} \cdot \frac{1}{2} = \frac{1}{2}.
 \end{array}$$

Now  $cp$  has been shown to be  $68^\circ 18'$ ; therefore:

$$\tan ms = 1/2 \cot 68^\circ 18'. \quad ms = 11^\circ 15'.$$

Then

$$sp = mp - ms = 21^\circ 42' - 11^\circ 15' = 10^\circ 27'.$$

The mean measured values of  $ms$  and  $sp$  were  $11^\circ 14'$  and  $10^\circ 24'$ , differing only  $1'$  and  $3'$  respectively from the values just calculated.

Having now calculated all the positions of poles in the two diagonal diametral zones, we may next proceed to calculate the positions of the poles of the forms  $z$ ,  $r$ , and  $s$  in the arc-zones connecting them with the  $a$ -poles. The fourth of these arc-zones, including also  $e$ -poles, has already been calculated, namely, that involving the parametral form  $p = [111]$ . We have proved from the measurements that the symmetry is truly tetragonal, so that we have only to calculate one angle for each form, namely,  $az$ ,  $ar$ , and  $as$ , for when each of these is known the other angle  $zz$ ,  $rr$ , or  $ss$  is given by the symmetry. Hence we have only now three angles to calculate  $az$ ,  $ar$ , and  $as$ ; and we use in the three cases the three triangles formed by  $a = (100)$ ,  $m = (110)$ , and the pole  $z$ ,  $r$ , or  $s$  in question, in which the common side  $am$  is  $45^\circ$  and the angle at  $m$  is always  $90^\circ$ .

**To find  $az = (100) : (113)$ .**

Employing the triangle  $a = (100) : m = (110) : z = (113)$ , the other necessary known part of the triangle is the side  $mz$ , which we have found to be  $50^\circ 3'$ . From the Napierian diagram we deduce by Napier's rules that:

$$\cos az = \cos 50^\circ 3' \cos 45^\circ. \quad az = 63^\circ 0'.$$

Then:

$$zz = (113) : (\bar{1}13) = 2(90^\circ - 63^\circ) = 2 \times 27^\circ 0' = 54^\circ 0'.$$

These values for  $az$  and  $zz$  are identical with the mean measured values.

**To find  $ar = (100) : (335)$ .**

Similarly, the other necessary element of the triangle  $a = (100) : m = (110) : r = (335)$  is the side  $mr$ , which has already been shown to be  $33^\circ 33'$ . From the Napierian diagram we deduce:

$$\cos ar = \cos 33^\circ 33' \cos 45^\circ. \quad ar = 53^\circ 53\frac{1}{2}'.$$

Then:

$$rr = (335) : (\bar{3}35) = 2(90^\circ - 53^\circ 53\frac{1}{2}') = 2 \times 36^\circ 6\frac{1}{2}' = 72^\circ 13'.$$

The mean measured values of  $ar$  and  $rr$  were respectively  $53^\circ 52'$  and  $72^\circ 15'$ .

**To find  $as = (100) : (221)$ .**

Also similarly, in the triangle  $a = (100) : m = (110) : s = (221)$  the other known element besides  $am = 45^\circ$  and the right angle at  $m$  is  $ms$ , which we have found to be  $11^\circ 15'$ . From these data and the Napierian diagram we derive:

$$\cos as = \cos 11^\circ 15' \cos 45^\circ. \quad as = 46^\circ 5'.$$

Then:

$$ss = (221) : (\bar{2}21) = 2(90^\circ - 46^\circ 5') = 2 \times 43^\circ 55' = 87^\circ 50'.$$

The mean measured values of these angles  $as$  and  $ss$  were respectively  $46^\circ 6'$  and  $87^\circ 48'$ .

It now only remains to calculate one further set of four equal zones, each including a parallel pair of  $m$ -faces and four  $e$ -faces, and which are indicated on the projection by the four circular arcs joining the ends of the diagonal diameters  $mcm$  (the  $m$ -poles) with two  $e$ -poles, one on each crystallographic axial diameter. There are only two

different angles, the same two in all four zones, a fact proved by the measurements and which is in accordance with the tetragonal symmetry, namely,  $me$  and  $ee$ .

To find  $me = (110) : (101)$ .

We employ the triangle  $m = (110) : e = (101) : a = (100)$ , which has a right angle at  $a$ ; the side  $am$  is  $45^\circ$  and the side  $ae$  is the basal angle  $29^\circ 22'$ . Constructing the Napierian diagram, we at once derive from it by Napier's rules :

$$\cos me = \cos 29^\circ 22' \cos 45^\circ. \quad me = 51^\circ 57'.$$

$$\text{Then :} \quad ee = (101) : (0\bar{1}1) = 2(90^\circ - 51^\circ 57') = 2 \times 38^\circ 3' = 76^\circ 6'.$$

The mean measured values of  $me$  and  $ee$  respectively were  $51^\circ 56'$  and  $76^\circ 7'$ , only  $1'$  removed from the calculated value in each case.

This completes the calculations for this crystal of anatase; they have throughout been found to confirm the measurements in a most satisfactory manner. It will have been observed that the whole of the calculations have been carried through entirely by the use of Napier's rules for right-angled triangles, which, owing to the high degree of symmetry, have always been available, and the anharmonic ratio of four poles in a right-angled zone. They have illustrated well how simple such calculations really are, and yet they have been carried out to the full extent required by the very complete series of measurements made. The experience gained in working through such an example as is afforded by this crystal of anatase, so richly endowed with faces, will give the student of practical crystallography considerable confidence, and enable him to proceed to the calculations of crystals of a lower order of symmetry without feeling that any insuperable difficulties whatsoever lie before him. Such difficulties as may be found will equally rapidly disappear under the application of the few straightforward rules given in Chapter VII.

We now finally proceed to draw up the table of results for anatase.

#### TABLE OF RESULTS FOR CRYSTAL OF ANATASE, $\text{TiO}_2$ .

**Crystal-system :** Tetragonal. Class : 15, tetragonal holohedral.

**Habit :** Bipyramidal, very rich in faces, so developed that the general contour is nearly spherical.

**Ratio of axes :**  $a : c = 1 : 1.7771$ .

**Forms observed :**  $a = \{100\}$ ,  $m = \{110\}$ ,  $e = \{101\}$ ,  $p = \{111\}$ ,  $z = \{113\}$ ,  $r = \{335\}$ ,  $s = \{221\}$ .

No face of  $c = \{001\}$  developed, upper and lower apices of bipyramid  $z = \{113\}$  pointed.

**Interfacial angles :** These are tabulated in the following list, the basal angle employed in the calculations being marked with an asterisk.

[TABLE

## MORPHOLOGICAL ANGLES OF ANATASE.

Angle.	No. of Measurements.	Limits.	Mean observed.	Calculated.	Difference.
$\left\{ \begin{array}{l} aa=(100):(010) \\ am=(100):(110) \\ \text{or } (010):(110) \end{array} \right.$	4 4	89° 59'–90° 1' 45 0–45 1	90° 0' 45 0	90° 0' 45 0	0' 0
$\left\{ \begin{array}{l} ae=(100):(101) \\ \text{or } (010):(011) \\ ce=(001):(101) \\ \text{or } (001):(011) \\ ee=(101):(101) \end{array} \right.$	8 .. 4	29 16–29 28 .. 121 12–121 16	29 22 .. 121 15	* 60 38 121 16	.. .. 1
$\left\{ \begin{array}{l} cz=(001):(113) \\ zz=(113):(\bar{1}13) \\ zr=(113):(335) \\ rp=(335):(111) \\ cp=(001):(111) \\ ps=(111):(221) \\ sm=(221):(110) \\ pm=(111):(110) \\ cr=(001):(335) \\ rm=(335):(110) \\ zm=(113):(110) \end{array} \right.$	.. 4 8 6 .. 3 3 4 .. 6 6	.. 79 52–79 54 16 29–16 34 11 48–11 58 .. 10 20–10 27 11 10–11 18 21 36–21 42 .. 33 30–33 34 50 3–50 5	.. 79 53 16 31 11 52 .. 10 24 11 14 21 39 .. 33 32 50 4	39 57 79 54 16 30 11 51 68 18 10 27 11 15 21 42 56 27 33 33 50 3	.. 1 1 1 .. 3 1 3 .. 1 1
$\left\{ \begin{array}{l} ap=(100):(111) \\ \text{or } (010):(111) \\ pe=(111):(101) \\ \text{or } (111):(011) \\ pp=(111):(\bar{1}11) \\ \text{or } (111):(\bar{1}11) \end{array} \right.$	8 8 4	48 47–48 59 41 0–41 8 82 8–82 15	48 55 41 5 82 10	48 56 41 4 82 9	1 1 1
$\left\{ \begin{array}{l} az=(100):(113) \\ \text{or } (010):(113) \\ zz=(113):(\bar{1}13) \\ \text{or } (113):(\bar{1}13) \end{array} \right.$	8 4	62 57–63 4 53 59–54 1	63 0 54 0	63 0 54 0	0 0
$\left\{ \begin{array}{l} ar=(100):(335) \\ \text{or } (010):(335) \\ rr=(335):(335) \\ \text{or } (335):(335) \end{array} \right.$	8 4	53 48–53 56 72 12–72 18	53 52 72 15	53 53 72 13	1 2
$\left\{ \begin{array}{l} as=(100):(221) \\ \text{or } (010):(221) \\ ss=(221):(221) \\ \text{or } (221):(221) \end{array} \right.$	6 4	46 1–46 9 87 47–87 51	46 6 87 48	46 5 87 50	1 2
$\left\{ \begin{array}{l} me=(1\bar{1}0):(101) \\ ee=(101):(011) \end{array} \right.$	6 4	51 54–51 59 76 6–76 8	51 56 76 7	51 57 76 6	1 1

The excellent agreement between the observed and calculated values of the various interfacial angles set forth in the table, indicated by the fact that the maximum difference given in the last column is only 3 minutes, is most satisfactory, and is such as can only be expected from small crystals of a high order of perfection, possessed of brilliant and truly plane faces.



## CHAPTER XIV

### RHOMBIC OR ORTHORHOMBIC SYSTEM

**Three rectangular but unequal crystallographic axes. Characterised by the vertical axis being an axis of only digonal symmetry, in which two planes of symmetry may intersect and to which two other digonal symmetry axes may be perpendicular.**

It will be evident from the above statement of the conditions for orthorhombic symmetry that three classes are possible in this system,

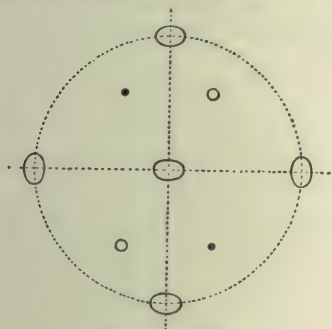


FIG. 178.—Class 6.

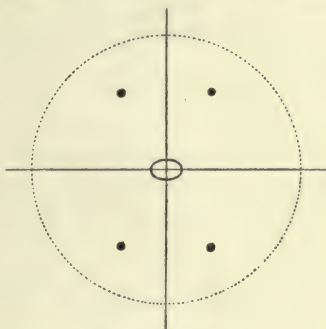


FIG. 179.—Class 7.

namely, one (class 7) in which the vertical crystallographic axis alone is a digonal axis, in which two planes of symmetry intersect; another (class 6) in which the other two crystallographic axes are also digonal axes, but in which no planes of symmetry are present; and a third (class 8) in which besides all three crystallographic axes being digonal axes they are also the lines of intersection of three rectangular symmetry planes. These three classes are comparatively indicated in their class order by the stereographic projections in Figs. 178, 179, and 180.

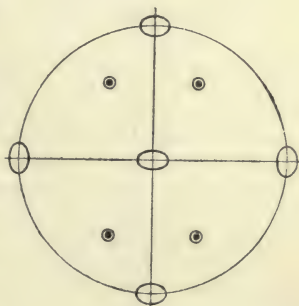


FIG. 180.—Class 8.

*Class 8.—Rhombic-Bipyramidal Class. Rhombic-Holohedral Class.  
Type, Di-Digonal Equatorial.*

In this, the highest class of orthorhombic symmetry, the three crystallographic axes are all digonal axes of symmetry, and they are the lines of intersection of three rectangular symmetry planes, identical with the three axial planes. The distinction from the cubic and tetragonal systems is that no two axes are of equal length, and no axis is one of pre-eminent symmetry, such as the principal axis of the tetragonal or hexagonal systems. Hence there is nothing to determine which axis shall be considered the vertical one, except in certain cases of analogy which will be referred to in a later chapter, but after a choice has been made of the vertical axis  $c$ , the longer of the two others is always taken as the lateral right-and-left axis  $b$ . This axis  $b$  is termed the macro-diagonal, and the shorter (front-and-back) axis  $a$  is termed the brachy-diagonal; the  $c$ -axis is simply referred to as the vertical axis.

The elements of symmetry and the general form  $\{hkl\}$  are shown in the stereographic projection, Fig. 180.

The general form, which is produced when the representative facial pole  $\{hkl\}$  falls within one of the eight equal octants into which the axial planes divide up the

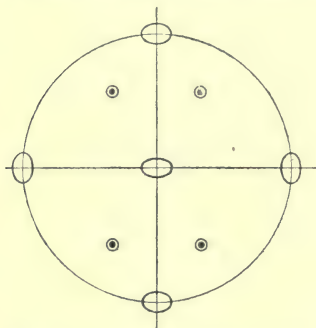


FIG. 180.—Symmetry Elements and General Form of Class 8.

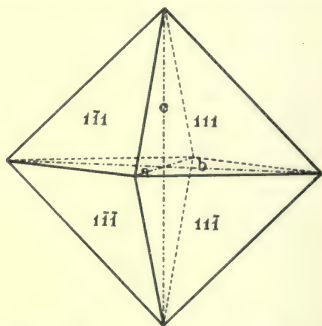


FIG. 181.—The Primary Rhombic Bipyramid.

sphere, consists, owing to the symmetrical repetition of the pole in all the other octants in accordance with the symmetry conditions, of an eight-faced bipyramid, the **rhombic bipyramid**, shown in Fig. 181, composed of two equal-faced and four-faced pyramids arranged base to base. The latter is a regular rhombus, the two pairs of opposite angles being of different magnitudes; in the case of the bipyramid chosen as the parametral form, that shown in Fig. 181, the more obtuse pair of angles are bisected by the brachy-diagonal and the acuter pair by the macro-diagonal. The particular primary rhombic bipyramid shown,  $\{111\}$ , is that of topaz, the ratio of the axes for which is  $a : b : c = 0.5287 : 1 : 0.9539$ . All the succeeding forms of this class shown in Figs. 182-186 are also those of topaz.

There are six special cases, each producing a specific form characteristic of the system. Three are open four-faced forms of prismatic type, and three are pinakoidal forms each composed of two parallel faces only. The first case

is when the typical pole ( $hkl$ ) lies on the primitive circle, intermediate between the ends of the axes. Repetition over the symmetry planes necessitates three other poles on the primitive circle, corresponding to the production of an open four-sided prism, parallel to the vertical axis, the **rhombic prism**; the parametral or primary form is  $\{110\}$ , the poles of which lie at the ends of the diameters passing through the poles of the parametral bipyramid, so that the section of the prism by the horizontal plane is like that of the latter. Of the general form  $\{hk0\}$ , the poles of which may lie on either side of these diameters, the macro-diagonal side or the brachy-diagonal side, there will be two corresponding types, which are sometimes distinguished as macro-prisms and brachy-prisms, just as are also termed macro- or brachy-pyramids such rhombic bipyramids other than the parametral one as have a macro- or brachy-character. There is no essential difference, however, in the

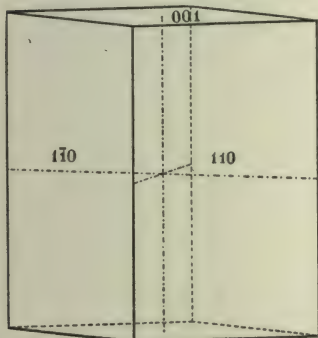


FIG. 182.—The Primary Rhombic Prism.

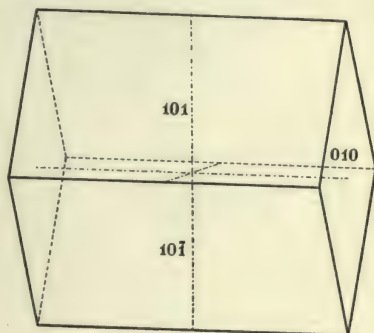


FIG. 183.—The Primary Macro-domal Prism.

type of form, so that there is little utility in the employment of these distinguishing terms, which, moreover, are much more properly used in another sense to be explained in the next paragraph. The primary rhombic prism  $\{110\}$  is shown in Fig. 182.

The second and third special cases occur when the pole ( $hkl$ ) migrates on to the diametral arcs  $ac$  or  $bc$  (see Fig. 196, page 232, for a typical rhombic stereographic projection). In the former case a form of four faces parallel to the macro-diagonal is produced, having the form symbol  $\{h0l\}$  and generally in the past called the **macro-dome**, but which may more correctly be termed the **macro-prism**, as it is another form of prismatic character. The term macro-prism has, however, already been appropriated by long usage (initiated by Naumann) for the four-faced prism of a macro-character parallel to the vertical axis as explained in the last paragraph; it is perhaps safest, therefore, and most free from ambiguity, to speak of the form  $\{h0l\}$  as the **macro-domal prism**, which term renders it quite plain to which type of form we refer. Its primary representative  $\{101\}$  is shown in Fig. 183.

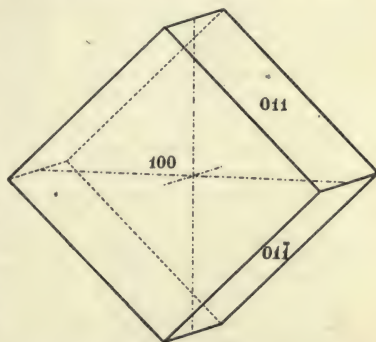


FIG. 184.—The Primary Brachy-domal Prism.

The third case, in which the pole lies on the arc  $bc$ , is that of a similar form of four prism-like faces parallel to the brachy-



diagonal, which similarly is best called the **brachy-domal prism**, its form symbol being  $\{0kl\}$ . Its primary representative  $\{011\}$  is shown in Fig. 184. These two forms correspond together to the tetragonal pyramid of the second order, and may be regarded as forming, when their intercepts on the  $c$  axis are alike, the rectangular rhombic bipyramid shown in Fig. 185. The two parts, parallel to the two lateral axes respectively, are, however, on account of the merely digonal character of rhombic symmetry, quite distinct forms.

The three remaining special cases are those when the pole  $\{hkl\}$  migrates to the ends of the axial diameters on the primitive circle or to the centre of the latter, comparable to the situations of the cube faces, or to those of the tetragonal prism of the second order and the basal plane. In the case of the rhombic system, however, the three pairs of parallel faces, which are thus parallel to the three axial planes, are three separate forms, namely, the **macro-pinakoid**  $\{100\}$  the poles of which are situated

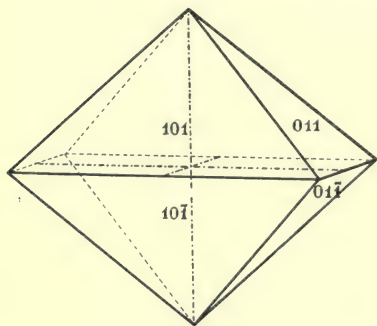


FIG. 185.—The Primary Rectangular Rhombic Bipyramid (two Forms).

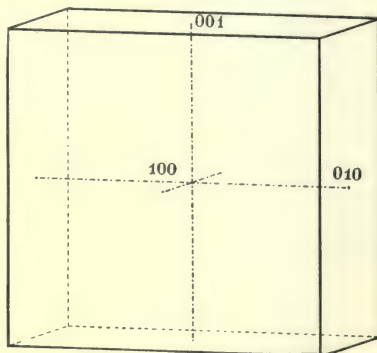


FIG. 186.—The Rectangular Rhombic Prism (three Forms).

at the ends of the axis  $a$ , the **brachy-pinakoid**  $\{010\}$  with poles at the terminals of the axis  $b$ , and the **basal pinakoid**  $\{001\}$  the poles of which occupy the centre of the projection.

The closed solid produced by the combination of these three primary forms is shown in Fig. 186. It is sometimes called a rectangular rhombic prism, each face being a rectangle, and the three edges meeting in each of the eight solid angles are parallel to the three crystallographic axes. The solid actually shown in Fig. 186 looks like a cube, but it is really drawn accurately to the scale of the axial system of topaz,  $a : b : c = 0.5287 : 1 : 0.9539$ ; the  $b$  and  $c$  axes appear to be equal, but they are really not so, being in the proportion of 1 to 0.9539.

The primary rhombic prism, primary macro-domal prism, and primary brachy-domal prism, are respectively shown in Figs. 182, 183, and 184 as closed by the basal pinakoid, the brachy-pinakoid, and the macro-pinakoid.

The forms possible to holohedral rhombic symmetry are thus seven in number, made up of the general bipyramid  $\{hkl\}$  and six special cases. They are comprised in the following list, in which not only are the above designations of the various forms given, but also those lately proposed for the rhombic, monoclinic and triclinic systems by Fedorov and adopted by von Groth, according to which the pinakoids are called "first," "second," or "third" when they are parallel to the three respective axial planes, and cut (perpendicularly in this system) the axes  $a$ ,  $b$ , and  $c$  respectively; while forms parallel to an axis are said to be of the first, second, or third "order" according as the axis is  $a$ ,  $b$ , or  $c$ .

*List of Forms in Class 8.*

- {001} Basal pinakoid ; or third pinakoid. 2 faces.
- {100} Macro-pinakoid ; or first pinakoid. 2 faces.
- {010} Brachy-pinakoid ; or second pinakoid. 2 faces.
- {hkl} Rhombic prisms, including the primary rhombic prism {110} ; or rhombic prisms of the third order. Each 4 faces.
- {h0l} Macro-domal prisms, including the primary macro-domal prism {101} ; or rhombic prisms of the second order. Each 4 faces.
- {0kl} Brachy-domal prisms, including the primary brachy-domal prism {011} ; or rhombic prisms of the first order. Each 4 faces.
- {hkl} Rhombic bipyramids, including the primary parametral rhombic bipyramid {111}. Each 8 faces.

Many excellent examples are available of substances crystallising in this holohedral class of the rhombic system, notably among natural minerals barytes, sulphate of barium  $\text{BaSO}_4$ , and topaz, fluoriferous silicate of aluminium  $(\text{AlF})_2\text{SiO}_4$ , a crystal of which will be fully described in the next chapter. Among chemical salts we have the sulphates of the alkali metals, of which one, sulphate of potassium,  $\text{K}_2\text{SO}_4$ , has already been fully worked out as a typical practical example of goniometry in Chapters IV. and VIII., and which is illustrated in Figs. 1, 2, and 3. The fairly complicated stereographic projection of potassium sulphate already given in Fig 38 (page 67) affords an excellent example of the projection of a holohedral rhombic crystal showing most of the types of forms above enumerated. Another example will be found in Fig. 196 on page 232, which represents the stereographic projection of the topaz crystal worked out as a further rhombic example.

*Class 7.—Rhombic-Pyramidal Class. Rhombic-Hemimorphic Class.*  
*Type, Digonal Polar.*

This class retains only one of the three digonal axes, which is conventionally placed vertically for descriptive purposes, and the two mutually rectangular planes of symmetry which intersect in it. The equatorial plane of symmetry thus disappears, together with the two digonal axes lying in it. The symmetry elements are shown in Fig. 187, together with the poles of the most general form {hkl}.

The latter is now only a single open **rhombic pyramid**, either an upper one with poles on the upper hemisphere as shown in the figure, or a lower one which would be represented if the dots were changed into rings. The rhombic prisms and macro- and brachy-pinakoids are the same as in the holohedral class 8, but the two parallel faces of the basal pinakoid now belong to separate forms, the upper and lower basal plane or "pedion," and Figs. 188 and 189 show two instances of an upper pyramid in combination with a basal plane. Fig. 188 represents

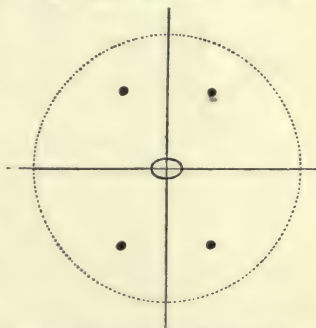


FIG. 187.—Symmetry Elements and General Form of Class 7.

the form  $\{321\}$ , and the shorter more obtuse one shown in Fig. 189 is  $\{123\}$ , both being constructed for the axial ratio of topaz,  $a : b : c = 0.5287 : 1 : 0.9539$ . The macro-domal and brachy-domal prisms are also divided into an upper and a lower macro-dome or hemi-prism and an upper and a lower brachy-dome or hemi-prism, and these forms are thus truly "domes" in this class, each consisting of two faces meeting in an edge.

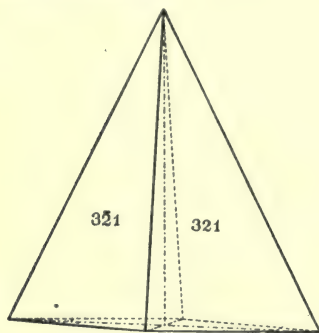


FIG. 188.  
Combinations of Upper Rhombic Pyramids with the Basal Plane.

The vertical axis  $c$  is obviously in this class a polar axis, for quite a different set of forms, pyramidal or domal, may be developed round one end of it than around the other end, and the two ends actually exhibit opposite pyro-electrical properties in the

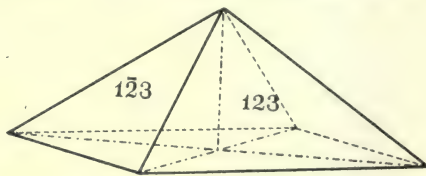


FIG. 189.

cases of the substances known to crystallise in the class.

We have, therefore, in résumé, the following forms in this class :

*List of Forms in Class 7.*

- $\{001\}$  Upper basal plane ; or upper third pedion. 1 face.
- $\{00\bar{1}\}$  Lower basal plane ; or lower third pedion. 1 face.
- $\{100\}$  Macro-pinakoid ; or first pinakoid. 2 faces.
- $\{010\}$  Brachy-pinakoid ; or second pinakoid. 2 faces.
- $\{hko\}$  Rhombic prisms, including the primary prism  $\{110\}$  : or rhombic prisms of the third order. Each 4 faces.
- $\{h0l\}$  Upper macro-domes or hemi-prisms, including the primary  $\{101\}$  ; or upper domes of the second order. 2 faces.
- $\{h0\bar{l}\}$  Lower macro-domes or hemi-prisms, including the primary  $\{10\bar{1}\}$  ; or lower domes of the second order. 2 faces.
- $\{0kl\}$  Upper brachy-domes or hemi-prisms, including the primary  $\{011\}$  : or upper domes of the first order. 2 faces.
- $\{0k\bar{l}\}$  Lower brachy-domes or hemi-prisms, including the primary  $\{01\bar{1}\}$  or lower domes of the first order. 2 faces.
- $\{hkl\}$  Upper rhombic pyramids, including the primary  $\{111\}$ . 4 faces.
- $\{hk\bar{l}\}$  Lower rhombic pyramids, including the primary  $\{11\bar{1}\}$ . 4 faces.

Hemimorphite, silicate of zinc,  $\text{Zn}_2\text{SiO}_3(\text{OH})_2$ , is an excellent example of a substance crystallising in this class. Fig. 190 represents a crystal of this mineral, which consists of a combination of the macro-pinakoid  $\{100\}$ , the brachy-pinakoid  $\{010\}$ , and the primary

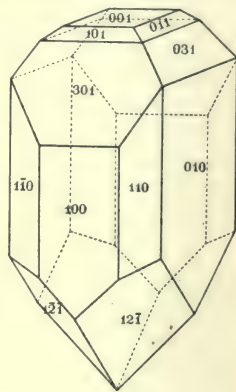


FIG. 190.  
Crystal of Hemimorphite.



prism  $\{110\}$ , together with the following terminal forms: At the upper termination, the "analogous" pyro-electrical pole (becoming positively charged on warming and negatively on cooling, the charge being analogous to the sign of the change of temperature), there are the macro-domes or hemi-prisms  $\{101\}$  and  $\{301\}$ , the brachy-domes or hemi-prisms  $\{011\}$  and  $\{031\}$ , and the upper basal plane  $\{001\}$ ; while at the lower end, the "antilogous" pyro-electrical pole (becoming negatively charged on warming and positively on cooling), only the single pyramid  $\{12\bar{1}\}$  is developed. The ratio of the axes, in accordance with which the figure is accurately drawn, is:— $a : b : c = 0.7835 : 1 : 0.4778$ , derived from the measurements of Schrauf. Etched figures on the brachy-pinakoid exhibit the polarity of the two ends very clearly. Hemimorphite is a basic silicate, and not a hydrated one; for the crystals withstand a rise of temperature up to  $340^{\circ}\text{C}$ . without change.

*Class 6.—Rhombic-Bisphenoidal Class. Rhombic-Hemihedral Class.  
Type, Digonal Holoaxial.*

This class possesses the full number of digonal axes of symmetry of the system, namely, three, identical with the three unequal rectangular crystallographic axes; there are no planes of symmetry present at all, however. Fig. 191 shows the symmetry elements and the general form  $\{hkl\}$ .

This latter is a four-faced figure corresponding to the tetragonal bisphenoid, and to the regular tetrahedron, but owing to the inequality of the axes its faces are scalene triangles instead of isosceles or equilateral. It is termed the **rhombic bisphenoid**. In the stereographic projection that particular bisphenoid is shown to which the face  $\{hkl\}$  belongs, situated in the top right front octant. Only alternate octants exhibit poles, so that there is a second possible bisphenoid the poles of which would occupy those octants which are unoccupied in the projection of the form shown, and the projection of which would be produced if the two dots were replaced by rings and the two rings by dots. This second form of rhombic bisphenoid is a distinct solid, the mirror-image of the first one, that is, the enantiomorph of the latter. Figs. 192 and 193 show the two bisphenoids side by side, the first form  $\{hkl\}$ , termed the right rhombic bisphenoid, in Fig. 192, and the second form  $\{h\bar{k}l\}$ , called the left rhombic bisphenoid, in Fig. 193. The two solids cannot be brought into coincidence or identity by any amount of rotation. The actual forms shown are  $\{321\}$  and  $\{3\bar{2}1\}$ , constructed for the axial ratio of topaz, the two together thus corresponding to the rhombic bipyramid  $\{321\}$ , of which the upper half is shown in Fig. 188.

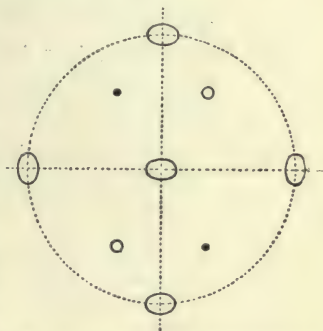


FIG. 191.—Symmetry Elements and General Form of Class 6.

The six possible special cases lead to no other new forms, but only to the same forms as in the holohedral class 8, namely, the two vertical pinakoids, basal pinakoid,

rhombic prisms, macro-domal and brachy-domal prisms. The following is, therefore, a summary of the possible forms in the class :

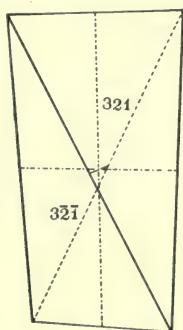


FIG. 192.

Right and Left Rhombic Bisphenoids.

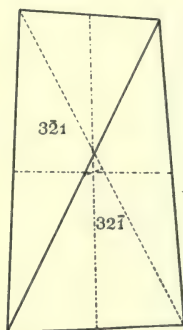


FIG. 193.

*List of Forms in Class 6.*

- $\{001\}$  Basal pinakoid ; or third pinakoid. 2 faces.
- $\{100\}$  Macro-pinakoid ; or first pinakoid. 2 faces.
- $\{010\}$  Brachy-pinakoid ; or second pinakoid. 2 faces.

- $\{h k 0\}$  Rhombic prisms, including the primary  $\{110\}$  ; or rhombic prisms of the third order. Each 4 faces.

- $\{h 0 l\}$  Macro-domal prisms, including the primary  $\{101\}$  ; or rhombic prisms of the second order. Each 4 faces.

- $\{0 k l\}$  Brachy-domal prisms, including the primary  $\{011\}$  ; or rhombic prisms of the first order. Each 4 faces.

- $\{h k l\}$  Right rhombic bisphenoid ;  $\{h \bar{k} l\}$  left rhombic bisphenoid ;  $\{111\}$  and  $\{1\bar{1}1\}$  are the right and left primary rhombic bisphenoids. Each 4 faces.

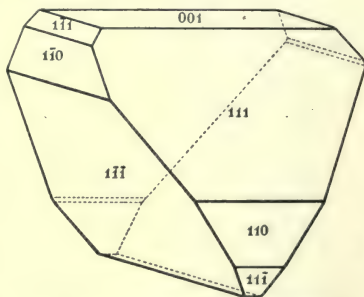


FIG. 194.—Crystal of Tartar-Emetic.

The well-known salt, tartar emetic, potassium antimonyl tartrate,  $K(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$ , crystallises in this class, and Fig. 194 shows a crystal of it exhibiting the two primary bisphenoids  $\{111\}$  and  $\{1\bar{1}1\}$ , developed to very different extents, in combination with the basal pinakoid  $\{001\}$  and the primary prism  $\{110\}$ .

Two other very important tartrates, which exhibit the enantiomorphism of this class 6 very clearly, and which will be considerably referred to in Chapters L. and LV., are potassium sodium tartrate, Rochelle or Seignette salt (see footnote on page 14),  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ , and sodium ammonium tartrate (ammonium Seignette salt),  $\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ . The two varieties of the latter salt were isolated by Pasteur.

## CHAPTER XV

### PRACTICAL EXAMPLE OF A RHOMBIC CRYSTAL

#### *Class 8.—Rhombic Holohedral. Topaz, $(AlF)_2SiO_4$ .*

ONE example of this system has already been fully worked out in Chapters IV. and VIII., namely, potassium sulphate, which also belongs to the holohedral class 8. It has been thought advisable, however, to include another example of this very important class of crystals, taken this time from among naturally occurring mineral substances and involving different problems, and topaz has been chosen because of the comparative ease with which excellent small crystals, suitable for goniometrical investigation, may be obtained.

The crystal of topaz employed as this example was somewhat larger than is usually chosen for goniometrical measurement, but the faces were so perfect and the signal-images afforded by them so truly excellent as a rule, that the crystal was found admirably suitable for our purpose. Its general appearance will be gathered from Fig. 195, and its stereographic projection is given in Fig. 196, the method of constructing which will be elaborated during the course of the chapter.

The crystal was a short prism, the prism zone exhibiting eight well-developed faces; it was terminated below only by a cleavage face parallel to the basal pinakoid, but above by an excellent natural face of the same form,  $c = \{001\}$ , and between this and the prism faces numerous facets of other forms were developed.

A preliminary study of the crystal had made it clear that the faces present were all those of forms known to be characteristic of topaz, a mineral which has been very thoroughly studied. Different observers have all agreed that the prism faces marked  $p$  shall be chosen as

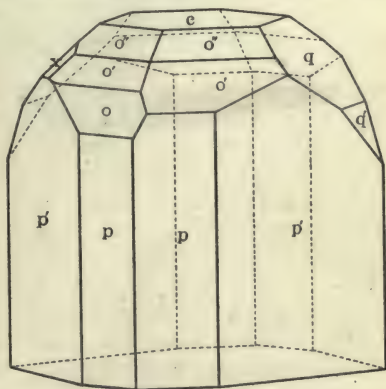


FIG. 195.—The Measured Crystal of Topaz.



those of the primary prism  $\{110\}$ , and the other four prism faces, marked  $p'$ , from their position with respect to the  $p$ -faces, become then those of the prismatic form  $\{120\}$ , as will be fully proved later on. The macro- and brachy-pinakoids are not usually present and were not developed on the crystal in question.

Between the basal pinakoid  $c=\{001\}$  and the prism  $p=\{110\}$  the faces of three different pyramids were developed, namely, those marked  $o$ ,

$o'$ , and  $o''$ . Of these the first is taken by von Kokscharow, and accepted by von Groth, as the parametral form  $o=\{111\}$ , but Miers takes the second,  $o'$ , as  $\{111\}$ . There is considerable ground for so doing, for  $o'$  is much more frequently developed than  $o$ , and on the crystal in question only one  $o$ -face, although a very large and well-developed one, was present. We shall adhere, however, to

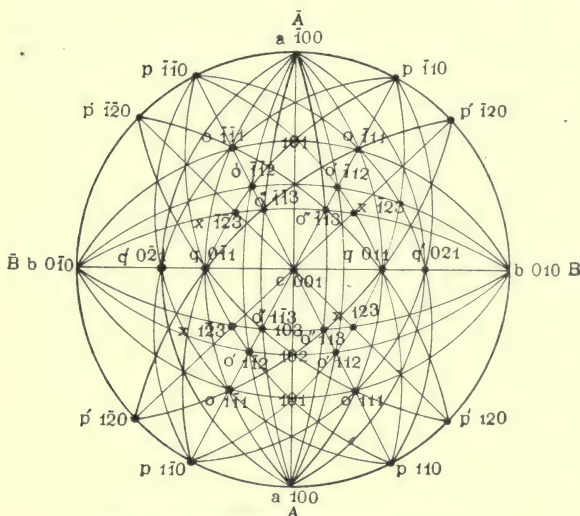


FIG. 196.—Stereographic Projection of Topaz.

the original mode of description by von Kokscharow, but as it will form an excellent exercise for the student to work out the whole of the facial symbols on the second plan, a comparison of the two modes of description will be made at the conclusion of the chapter, after the presentation of the results of the measurements and calculations. There is no cleavage other than the principal one parallel to the basal plane to guide us in the choice of the plane which shall determine the length of the vertical axis, so that there is equal ground for choosing either the  $o$ -faces or the  $o'$ -faces as the parametral ones. Assuming for the purposes of the description, however, that  $o$  is  $\{111\}$ , the form  $o'$  will be shown from its position to be  $\{112\}$ , and the form  $o''$  to be  $\{113\}$ .

There were also developed the faces of two different forms between the basal pinakoid and the possible brachy-pinakoid  $b=\{010\}$ , namely the primary and secondary brachy-domal prisms  $q=\{011\}$  and  $q'=\{021\}$ . In addition, there was one face present on the crystal of a pyramidal form in the zone  $[c=\{001\}, p'=\{120\}]$ , namely,  $x=\{123\}$ . All the letters representing these forms are those adopted by von Groth from von Kokscharow.

It will obviously be an advantage to commence with the measurement of the prism zone. The crystal was set up on the wax cone of the goniometer by its broad

basal cleavage plane, and the zone of prism faces adjusted in the usual manner, by arranging one of them parallel to one of the adjusting movements, and then adjusting the signal-images from that face and an adjoining one by means of the two adjusting screws. The whole eight faces belonging to the zone were then found to be automatically adjusted, and gave the following measurements :

## PRISM ZONE.

Circle Readings.	Angles.
$p$ 360° 0'A	$pp$ 55° 43'A
$p$ 304 17 A	$pp'$ 18 47
$p'$ 285 30	$p'p'$ 86 50
$p'$ 198 40	$p'p$ 18 44
$p$ 179 56 A	$pp$ 55 45 A
$p$ 124 11 A	$pp'$ 18 45 A
$p'$ 105 26 A	$p'p'$ 86 46 A
$p'$ 18 40 A	$p'p$ 18 42 A
$p$ 359 58 A	

The absence of the macro- and brachy-pinakoids renders the proof of the symmetry, with respect to the two axial planes of symmetry intersecting in the vertical axis, not so immediately clear as would be the case if they were present. For it is not yet apparent that the angles  $pp$  and  $p'p'$  are bisected by the normals to the possible macro-pinakoid  $a = \{100\}$  and brachy-pinakoid  $b = \{010\}$ , and for all the immediate evidence the prism zone alone offers, the positions of the whole of the poles might be rotated together anywhere about the vertical axis so long as the relationships indicated by the measurements were retained. As topaz is so well known, however, we may at once set forth the poles at the measured angles along the primitive circle, beginning with the  $p$ -poles at the distance from the possible  $a$ -poles of half the angle  $pp$ , and with the  $p'$  poles distant from the possible  $b$ -poles by half the angle  $p'p'$ . For it will be abundantly shown by the measurements of further zones that the symmetry thus given to the poles of the prism zone is correct.

The fact that the pair of values for  $pp$  are practically identical, and that the two  $p'p'$  values are similarly within the limits of error allowed for equal angles, does not tell us anything more than that parallel faces are concerned in the angles. But the fact that the four values of  $pp'$  are also evidently intended to be equal, the "A" values being within the prescribed limits, is much more significant, for it indicates that the angles in the four quadrants of the primitive circle are equal, an indication of probable rhombic or at least monoclinic symmetry.

We may now tabulate the values of like angles and take the mean in each of the three cases as representing the most probable true value of the angle. The means were  $pp = 55^\circ 44'$ ,  $pp' = 18^\circ 44'$ , and  $p'p' = 86^\circ 48'$ .

We may proceed next to measure the three zones perpendicular to the prism zone, all of which contain the basal pinakoid as the best-developed face. Two of these are obviously of similar character, namely the zones  $[co'o'p]$ , while the third is apparently different, namely, the zone  $[cqq']$ . It will therefore be most convenient to measure the latter zone first.

The crystal was fixed on the wax cone of the goniometer by the two front  $p$ -faces, the prism axis being arranged horizontally and the  $c$ -faces vertically and parallel to one of the adjusting screws. On adjusting the signal-image from one of these  $c$ -faces and that from an adjacent  $q$ -face by means of the two screws, the zone of faces in automatic adjustment was found to consist of a pair of  $q$ -faces, a pair of  $q'$ -faces, and the  $c$ -face and its parallel cleavage face. The measurements afforded were as under :

## BRACHY-DOMAL PRISM ZONE.

Circle Reading.	Angle.
$\left\{ \begin{array}{l} q' \ 360^\circ \ 0' \ A \\ q \ 341 \ 21 \ A \\ c \ 297 \ 42 \ A \\ q \ 254 \ 3 \ A \\ q' \ 235 \ 22 \ A \end{array} \right.$	$\left\{ \begin{array}{l} q'q \ 18^\circ \ 39' \ A \\ qc \ 43 \ 39 \ A \\ cq \ 43 \ 39 \ A \\ qq' \ 18 \ 41 \ A \end{array} \right.$

The signal-images were all truly excellent, and the angular values afforded leave no doubt whatever that the zone is symmetrical to the axial plane parallel to the possible brachy-pinakoid  $b=\{010\}$ . The angle  $cq$  is  $43^\circ 39'$ , two identical values having been obtained for the two similar angles on the two sides of the basal pinakoid ; and the angle  $qq'$  may be safely taken to be  $18^\circ 40'$ , the mean being undoubtedly legitimate to take, as the individual values are only  $2'$  apart, and thus within the prescribed limits for identical angles.

We may consequently draw in the zone  $[cq q']$  as the horizontal diameter of the primitive circle of the stereographic projection, bisecting the angle  $p'p'$ , the terminations being the possible brachy-pinakoid poles  $b=(010)$  and  $b=(0\bar{1}0)$ ; and we may put in the poles  $q$  and  $q'$  at their proper positions—by the usual process of drawing a perpendicular diameter, which will pass through  $a=(100)$ ,  $c=(001)$ , and  $a=(\bar{1}00)$ , and which in this case should anyhow be shown in the drawing as it is the projection of the axial plane parallel to the brachy-pinakoid—marking off the angles  $cq$  and  $cq'$  from the top end  $a=(\bar{1}00)$  of this latter diameter, along the primitive circle, and joining the points thus marked off to the lower end  $a=(100)$  of the diameter, which is the pole of the zone  $[cq q']$ . The points where the junction lines intersect the diameter  $b=(010)$ ,  $c=(001)$ ,  $b=(0\bar{1}0)$ , are the required poles  $q$  and  $q'$ . It will presently be proved that the position of the zone is symmetrical to the prism faces  $p$  and  $p'$ , that is, that the diameter  $[cq q'b]$  does bisect the angle  $p'p'$ .

We next measure the pair of apparently similar zones  $[co''o'p]$ .

The crystal may be reset on the wax, maintaining the  $c$ -faces vertical and parallel to an adjusting screw, but with the edges  $cq$  and  $qq'$  now horizontal instead of vertical. By use of the other adjusting screw, first on one side of the centre and then on the other, each of the two zones in question may in turn be adjusted so that the edges  $co''$  and  $o''o'$  are vertical, and the two zones thus successively measured. The actual measurements obtained were as follows :

[TABLE



## 2 SIMILAR DIAMETRAL PYRAMIDAL ZONES.

Circle Readings.	Angles.	Circle Readings.	Angles.
$\left\{ \begin{array}{l} p \ 360^\circ \ 0'A \\ o \ 333 \ 52 \ A \\ o' \ 315 \ 35 \ A \\ o'' \ 304 \ 15 \ A \\ c \ 270 \ 2 \ A \\ o'' \ 235 \ 46 \ A \\ o' \ 224 \ 26 \ A \\ p \ 180 \ 2 \ A \end{array} \right.$	$\left\{ \begin{array}{l} po \ 26^\circ \ 8'A \\ oo' \ 18 \ 17 \ A \\ po' \ 44 \ 25 \ A \\ o'o'' \ 11 \ 20 \ A \\ o''c \ 34 \ 13 \ A \\ co'' \ 34 \ 16 \ A \\ o''o' \ 11 \ 20 \ A \\ o'p \ 44 \ 24 \ A \end{array} \right.$	$\left\{ \begin{array}{l} p \ 360^\circ \ 0'A \\ o' \ 315 \ 35 \ A \\ o'' \ 304 \ 14 \ A \\ c \ 269 \ 59 \ A \\ o'' \ 235 \ 46 \ A \\ o' \ 224 \ 27 \ A \\ p \ 180 \ 2 \ A \end{array} \right.$	$\left\{ \begin{array}{l} po' \ 44^\circ \ 25'A \\ o'o'' \ 11 \ 21 \ A \\ o''c \ 34 \ 15 \ A \\ co'' \ 34 \ 13 \ A \\ o''o' \ 11 \ 19 \ A \\ o'p \ 44 \ 25 \ A \end{array} \right.$

Collecting now the measured values of the angles of the two zones which appear to be similar, it becomes clear that the four values of each of the angles  $co''$ ,  $o''o'$ ,  $o'p$ , and  $co'$  are within the accepted limits for identity,  $o'p$  only showing 1' difference and  $co'$ , for which the greatest difference occurs, only 4'. Hence we can legitimately conclude that the angles between the basal pinakoid and the four  $o''$  faces, or between the basal pinakoid and the four  $o'$  faces, are equal, and this involves not only symmetry with respect to the two vertical axial planes parallel to  $a=\{100\}$  and  $b=\{010\}$  but also symmetry with respect to the horizontal axial plane  $c=\{001\}$ , in short, full rhombic symmetry. The mean of the four values of each of the four angles just referred to may therefore be taken. They are:  $co''=34^\circ 14'$ ,  $o''o'=11^\circ 20'$ ,  $o'p=44^\circ 25'$ , and  $co'=45^\circ 34'$ . If the crystal were a doubly terminated one, instead of being only singly terminated, a precisely similar arrangement of faces would occur in the lower hemisphere as in the upper one measured, because to every face on the upper hemisphere there would correspond a parallel one in the lower hemisphere, and all poles but those of the primitive circle might thus have rings placed round the dots to represent this fact. Only one face of the primary pyramid  $o$  was present, namely  $(1\bar{1}1)$ , but it was quite a large and brilliant one, affording an excellent image of the signal. The values found for  $po$  and  $oo'$  were  $26^\circ 8'$  and  $18^\circ 17'$ .

The poles  $o$ ,  $o'$ , and  $o''$  may now be inserted in their proper places in the stereographic projection, on the two diameters  $pcp$ , by the same usual method as in the cases of the  $q$  and  $q'$  poles, the perpendicular diameters required in the construction not being left permanently in, however, after their use as containing the poles of the  $pcp$  zones, as they are not zonal diameters. It is only necessary to find the position of one  $o$ , one  $o'$ , and one  $o''$  pole, for all the others are similar, and can be marked off with the compasses at the same distances from the centre  $c$ .

There is one further diametral zone to be measured, namely, that containing the only developed face of the form  $x$ , the indices of which will presently be proved to be  $\{123\}$ . This face was  $(1\bar{2}3)$ , and it lay in the same zone with, and between, the basal pinakoid  $c=\{001\}$  and the prism-face  $p'=(1\bar{2}0)$ .

DIAMETRAL ZONE CONTAINING  $x = \{123\}$ .

Circle Readings.

Angles.

$$\begin{cases} c & 360^\circ & 0'A \\ x & 318 & 45 \\ p' & 270 & 0 A \end{cases}$$

$$\begin{cases} cx & 41^\circ & 15' \\ xp' & 48 & 45 \end{cases}$$

The position of the pole of this  $x$ -face on the diameter  $cxp'$  of the projection should next be found, as for the  $o$  and  $q$  poles, and the dot inserted to mark it.

In further test of the symmetry we ought next to measure all the arc-zones which may be drawn from the poles  $a$  and  $b$ , at the ends of the axial diameters, to pass respectively through a pair of the poles of each pyramid, that is, through two  $o$ -poles, two  $o'$ -poles, and two  $o''$ -poles. There will be three such arc-zones on each side of each axial diameter, thus making twelve altogether. As, however, only one face of the primary pyramid  $o = \{111\}$  is developed, and no  $a = \{100\}$  or  $b = \{010\}$  faces are present, the four zones involving the primary pyramid cannot be measured, except as regards one angle between the single  $o$  face ( $1\bar{1}1$ ) and the adjacent  $q$  face ( $0\bar{1}1$ ), and the other angles in this zone can only be determined by calculation, an excellent example of the use of the calculations. Hence, the zones of this type to be measured reduce to eight, or nine if we include the single measurement of  $oq$ , and the actual measurements obtained with them are now given below. In one of them the single face of the pyramid  $x = \{123\}$  occurs.

Circle Readings.	Angles.	Circle Readings.	Angles.
2 ZONES [ $ao''o''a$ ]		2 ZONES [ $ao'o'a$ ]	
$\begin{cases} o'' & 59^\circ & 42'A \\ o'' & 0 & 0 A \end{cases}$	$o''o'' 59^\circ 42'A$	$\begin{cases} o' & 78^\circ & 20'A \\ o' & 0 & 0 A \end{cases}$	$o'o' 78^\circ 20'A$
$\begin{cases} o'' & 59^\circ & 37' \\ o'' & 0 & 0 A \end{cases}$	$o''o'' 59^\circ 37'$ Mean $59^\circ 39\frac{1}{2}'$	$\begin{cases} o' & 78^\circ & 18' \\ o' & 0 & 0 A \end{cases}$	$o'o' 78^\circ 18'$ Mean $78^\circ 19'$
2 ZONES [ $bo''o''b$ ]		2 ZONES [ $bo'o'b$ ]	
$\begin{cases} x & 43^\circ & 50' \\ o'' & 30 & 29 A \\ o'' & 0 & 0 A \end{cases}$	$xo'' 13^\circ 21'$ $o''o'' 30 29 A$	$\begin{cases} o' & 39^\circ & 0'A \\ o' & 0 & 0 A \end{cases}$	$o'o' 39^\circ 0'A$
$\begin{cases} o'' & 30^\circ & 29'A \\ o'' & 0 & 0 A \end{cases}$	$o''o'' 30^\circ 29'A$ Mean $30^\circ 29'$	$\begin{cases} o' & 39^\circ & 3'A \\ o' & 0 & 0 A \end{cases}$	$o'o' 39^\circ 3'A$ Mean $39^\circ 1\frac{1}{2}'$

It will be obvious that the two individual values for each pair of angles belonging to the two similar arc-zones on the two sides of an axial diameter are within the limits for intended equality, and that the measurement of these arc-zones fully confirms the supposition that the axial diameters are the projections of planes of symmetry.

The measurement of the angle between the only developed  $o$ -face ( $1\bar{1}1$ ) and the adjacent  $q$ -face ( $0\bar{1}1$ ) gave the following result :

Circle Readings.

Angle.

$$\begin{cases} o & 52^\circ 30' \\ q & 0 \quad 0 \text{ A} \end{cases}$$
 $oq \ 52^\circ 30'$ 

These circular arc-zones should all be drawn in the projection, by the usual process of constructing a circular arc to pass through three points.

We may conclude the measurements with two pairs of arc-zones drawn from the ends of each of the  $cp$  diameters and one pair drawn from the ends of the  $cp'$  diameters, namely, the zones  $[pqo'p]$ ,  $[pq'op]$ , and  $[p'oo''qp']$ . All four of the repetitions of the first of these zones were measured, and gave the following angular values :

4 ZONES  $[pqo'p]$ .2 terminating each at  $p=(110)$  and  $p=(\bar{1}10)$ .2 terminating each at  $p=(1\bar{1}0)$  and  $p=(\bar{1}10)$ .

Circle Readings.	Angles.	Circle Readings.	Angles.
$\begin{cases} p & 360^\circ \ 0 \text{ A} \\ q & 288 \ 50 \text{ A} \\ o' & 246 \ 20 \text{ A} \\ p & 180 \ 0 \text{ A} \end{cases}$	$\begin{cases} pq & 71^\circ 10' \text{ A} \\ qo' & 42 \ 30 \text{ A} \\ o'p & 66 \ 20 \text{ A} \end{cases}$	$\begin{cases} p & 360^\circ \ 0 \text{ A} \\ q & 288 \ 49 \text{ A} \\ o' & 246 \ 18 \text{ A} \\ p & 180 \ 0 \text{ A} \end{cases}$	$\begin{cases} pq & 71^\circ 11' \text{ A} \\ qo' & 42 \ 31 \text{ A} \\ o'p & 66 \ 18 \text{ A} \end{cases}$
$\begin{cases} p & 180^\circ \ 0 \text{ A} \\ o' & 113 \ 46 \text{ A} \\ x & 100 \ 12 \\ q & 71 \ 12 \text{ A} \\ p & 0 \ 0 \text{ A} \end{cases}$	$\begin{cases} po' & 66^\circ 14' \text{ A} \\ o'x & 13 \ 34 \\ xq & 29 \ 0 \\ o'q & 42 \ 34 \text{ A} \\ qp & 71 \ 12 \text{ A} \end{cases}$	$\begin{cases} p & 180^\circ \ 0 \text{ A} \\ o' & 113 \ 41 \text{ A} \\ q & 71 \ 12 \text{ A} \\ p & 0 \ 0 \text{ A} \end{cases}$	$\begin{cases} po' & 66^\circ 19' \text{ A} \\ o'q & 42 \ 29 \text{ A} \\ qp & 71 \ 12 \text{ A} \end{cases}$

It will be evident that the four individual values for each of the angles  $pq$ ,  $qo'$ , and  $o'p$  are intended to be equal, that is, that these four different angles on the crystal in each case are of equal value as regards the symmetry. The differences in the case of the first,  $pq$ , are only 2', so that the mean  $71^\circ 11'$  can be accepted without hesitation as the true value. In the case of the other two angles,  $qo'$  and  $o'p$ , the differences reach 5' and 6', but the evidence is now so strong that rhombic symmetry is present that here too we are quite justified in regarding the mean values,  $qo'=42^\circ 31'$  and  $o'p=66^\circ 18'$ , as the expression of the truth, especially as two pairs of the values only differ by 1' and 2'. It will be observed that the face  $x=(1\bar{2}3)$  belongs to one of these four similar zones, and the values of the angles  $qx=29^\circ 0'$  and  $xo'=13^\circ 34'$  are quite trustworthy, although they depend on a single measurement in each case.

The circular arcs representing these zones should be constructed on the projection in the usual manner already above referred to.

Of the four possible repetitions of each of the other two zones  $[pq'op]$  and  $[p'oo''qp']$  only one in each case was measured, namely, that one which included the only developed  $o$ -face. The readings are as follows :



Circle Readings.	Angles.	Circle Readings.	Angles.
$\left\{ \begin{array}{ll} p & 360^\circ \quad 0' A \\ q' & 294 \quad 27 A \\ o & 239 \quad 40 A \\ p & 180 \quad 0 A \end{array} \right.$	$\left\{ \begin{array}{ll} pq' & 65^\circ \quad 33' A \\ q'o & 54 \quad 47 A \\ op & 59 \quad 40 A \end{array} \right.$	$\left\{ \begin{array}{ll} p' & 180^\circ \quad 0' A \\ o & 148 \quad 14 A \\ o'' & 98 \quad 42 A \\ q & 59 \quad 54 A \\ p' & 0 \quad 0 A \end{array} \right.$	$\left\{ \begin{array}{ll} p'o & 31^\circ \quad 46' A \\ oo'' & 49 \quad 32 A \\ o''q & 38 \quad 48 A \\ qp' & 59 \quad 54 A \end{array} \right.$

The circular arcs representing these two zones on the stereographic projection, terminating respectively at  $p=(110)$  and  $p'=(\bar{1}\bar{1}0)$  in one case and at  $p'=(1\bar{2}0)$  and  $p'=(\bar{1}20)$  in the other, and also the two similar zones terminating at the other pairs of  $p$  and  $p'$  poles, should be constructed, the centres being found in the usual manner for any circular arc on which at least three points are given. This will then complete the stereographic projection, and a fully adequate number of measurements have also now been made to secure a full description of the crystal, and for the determination of its symmetry and elements.

The measured angles should then be tabulated according to zones in their proper order, in the manner shown in the table of angles given at the end of this chapter, leaving a blank column for the subsequent insertion of the calculated values. The table should also indicate the number of measurements made of each angle, and the limiting values for each angle.

The measurements have fully confirmed our preliminary impression that the symmetry according to which the crystal is built up is rhombic. Having thus satisfied ourselves as to the symmetry, we may pass to the calculations, which will not only afford us confirmation of the indices imputed preliminarily to the faces of forms other than the axial planes and the primary parametral pyramid  $o=\{111\}$ , but will also give us the crystal elements, as well as enabling us to check the values of those angles the measurement of which was afforded by faces of less than the general excellence of facial development manifested by this truly magnificent crystal.

#### *Calculation of Angles and Elements.*

**Basal Angles.**—For the two essential basal angles it will be convenient to choose :

$$\begin{aligned} pp &= (110) : (1\bar{1}0) = 55^\circ 44' \\ cq &= (001) : (011) = 43^\circ 39'. \end{aligned}$$

Both angles were measured with particular trustworthiness, the two values of the former being only  $2'$  different, or only  $1'$  each from their mean, while the two values of the latter were identical with each other.

**Axial Ratios.**—The values of the ratios  $a:b$  and  $c:b$  are directly afforded by calculation from the two basal angles, for :

$$\begin{aligned} \frac{a}{b} &= \tan ap = \tan \frac{1}{2} pp = \tan 27^\circ 52'; \quad \frac{c}{b} = \tan cq = \tan 43^\circ 39'. \\ &= 0.5287 \qquad \qquad \qquad = 0.9539. \end{aligned}$$

Hence :  $a : b : c = 0.5287 : 1 : 0.9539$ .

These values for the axial ratios are practically identical with those given by von Kokscharow, which are  $0.5285 : 1 : 0.9539$ .

The proof that the ratio  $a : b = \tan ap$ , and that the ratio  $c : b = \tan cq$ , has already been shown to follow from the simplification of the general mode of calculating axial ratios (in the case of triclinic crystals) which is effected when the symmetry is rhombic and the axial angles become  $90^\circ$ . It is fully set forth in Chapter VII. page 112.

We may derive the proof directly from first principles, however, which is always more instructive when possible. For if we draw a diagram showing the conditions, as in Fig. 197, producing  $Oa$  to  $A$  and  $Ob$  to  $B$  to meet the tangent  $ApB$  drawn to the primitive circle of the stereographic projection at  $p$ , it will at once be seen that the angle  $AOp$ ,—the angle between the normals to  $a = (100)$  and  $p = (110)$ , and which is half the measured angle  $pp = (110) : (1\bar{1}0)$ , namely  $27^\circ 52'$ ,—is equal to the angle at  $B$  in  $AOB$ , and that the tangent of this angle at  $B$  is  $\frac{OA}{OB}$ . Now  $OA$  is the intercept on the axis  $a$  cut off by the primary prism face  $p = (110)$ , and  $OB$  is similarly the intercept on the axis  $b$  cut off by the same plane.

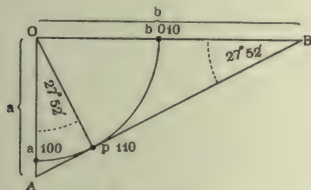


FIG. 197.

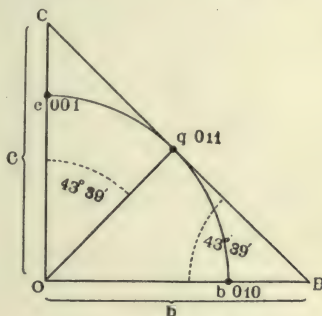


FIG. 198.

Hence :  $\frac{OA}{OB} = \frac{a}{b}$ , and therefore :  $\frac{a}{b} = \tan 27^\circ 52'$ .

Similarly, the primary brachy-prism face  $q = (011)$  cuts off the intercepts  $c$  and  $b$  from the vertical axis  $c$  and the horizontal right-and-left axis  $b$ , as shown in Fig. 198, and the angle at  $B$  gives the ratio of these intercepts, for its tangent  $\frac{OC}{OB} = \frac{c}{b}$ . Now the angle at  $B$  is equal to the angle  $COq$ , the angle between the normals to the faces  $c = (001)$  and  $q = (011)$ , which has been found by measurement to be  $43^\circ 39'$ . Hence :

$$\frac{c}{b} = \tan 43^\circ 39'.$$

### Calculation of Angles.

Commencing with the angles in the prism zone other than the basal angle  $ap$  :

**To find  $bp' = (010) : (120)$  and  $p'p = (120) : (110)$ .**

The pole  $p'$  is a fourth in the  $90^\circ$ -zone  $[app'b]$  in which we know the positions of the other three, so that we can conveniently employ the anharmonic ratio of four poles in a zone. Expressing the conditions diagrammatically as usual along a line (see Fig. 45 or Fig. 58 on pages 93 or 117) we can immediately deduce therefrom :

$$\frac{\sin ap}{\sin ap'} \cdot \frac{\sin bp'}{\sin bp} = \frac{100}{100} \cdot \frac{010}{010},$$

$$\frac{\sin 27^\circ 52'}{\cos bp'} \cdot \frac{\sin bp'}{\cos 27^\circ 52'} = \frac{1}{2} \cdot \frac{1}{1},$$

$$\tan bp' = \frac{1}{2} \cot 27^\circ 52'. \quad bp' = 43^\circ 24'.$$

Then :  $p'p = bp - bp' = 62^\circ 8' - 43^\circ 24' = 18^\circ 44'.$

This value for  $pp'$  is identical with the mean of the four measurements obtained of this angle.

We may next take the angles in the zone  $[cq q'b]$  other than the basal angle  $cq$ , namely :

To find  $bq' = (010) : (021)$  and  $q'q = (021) : (011).$

We employ the anharmonic ratio of four poles in a  $90^\circ$ -zone again, as in the last case, and from the conditions we have :

$$\frac{\sin cq}{\sin cq'} \cdot \frac{\sin bq'}{\sin bq} = \frac{001}{001} \cdot \frac{010}{010},$$

$$\frac{\sin 43^\circ 39'}{\cos bq'} \cdot \frac{\sin bq'}{\cos 43^\circ 39'} = \frac{1}{2} \cdot \frac{1}{1},$$

$$\tan bq' = \frac{1}{2} \cot 43^\circ 39'. \quad bq' = 27^\circ 40'.$$

Then :  $q'q = bq - bq' = 46^\circ 21' - 27^\circ 40' = 18^\circ 41'.$

The two measured values of this angle were  $18^\circ 39'$  and  $18^\circ 41'$ , which show a satisfactory agreement.

We may next proceed to find the angles in the zone  $[co''o'op]$  beginning with that of the primary pyramid  $o$ .

To find  $co = (001) : (111).$

The right-angled triangle  $c = (001)$ ,  $q = (011)$ ,  $o = (111)$  is convenient for this purpose. From the Napierian diagram, drawn as in Fig. 53, page 107, we derive :

$$\cos 62^\circ 8' = \cot co \tan 43^\circ 39',$$

or

$$\tan co = \frac{\tan 43^\circ 39'}{\cos 62^\circ 8'}. \quad co = 63^\circ 54'.$$

Then :  $op = 90^\circ - co = 90^\circ - 63^\circ 54' = 26^\circ 6'.$

The only measured value of  $co$  was  $63^\circ 50'$  and of  $op$   $26^\circ 8'.$

Having thus found the position of the primary pyramid we can find that of each of the others  $o'$  and  $o''$  by considering a pole of each in turn as the fourth pole in the  $90^\circ$ -zone  $[cop]$ , and employing the anharmonic ratio.

To find  $co' = (001) : (112).$

The conditions, set out in the usual linear diagram, enable us to form the ratio as follows :

$$\frac{\sin co'}{\sin co} \cdot \frac{\sin po}{\sin po'} = \frac{001}{001} \cdot \frac{110}{110},$$

$$\frac{\sin co'}{\sin 63^\circ 54'} \cdot \frac{\cos 63^\circ 54'}{\cos co'} = \frac{1}{1} \cdot \frac{1}{2},$$

$$\tan co' = \frac{1}{2} \tan 63^\circ 54'. \quad co' = 45^\circ 35'.$$



Then :  $o'p = 90^\circ - co' = 90^\circ - 45^\circ 35' = 44^\circ 25'$ .  
 Also :  $o'o = co - co' = 63^\circ 54' - 45^\circ 35' = 18^\circ 19'$ .

The mean measured value of  $co'$  was  $45^\circ 34'$  and of  $o'p$   $44^\circ 25'$ . The only measured value of  $o'o$  was  $18^\circ 17'$ .

To find  $co'' = (001) : (113)$ .

The position of  $o''$  can be found in a precisely similar manner, the pole  $o'' = (113)$  taking the place of  $o' = (112)$  in the anharmonic ratio just worked out. The only difference in the final form of the formula is that the 2 in  $\frac{1}{2}$  is replaced by 3, so that it reads as follows :

$$\tan co'' = \frac{1}{3} \tan 63^\circ 54'. \quad co'' = 34^\circ 14'.$$

Then :  $o''o' = co' - co'' = 45^\circ 35' - 34^\circ 14' = 11^\circ 21'$ .

The mean measured value for  $co''$  was identical with the above value, the most divergent individual values being only  $2'$  removed. The mean measured  $o''o'$  was  $11^\circ 20'$ , the outside individual values being  $1'$  on each side of this.

We next proceed to calculate the angles in the arc-zones terminating at the poles  $a$  and  $b$ .

To find  $ao = (100) : (111)$  and  $oq = (111) : (011)$ .

We can get  $qo$  from the right-angled triangle  $cqo$  already used for finding  $co$ . The Napierian diagram at once affords us the following equation in accordance with Napier's rules :

$$\sin qo = \sin 62^\circ 8' \sin 63^\circ 54'(co). \quad qo = 52^\circ 33'.$$

Then :  $ao = 90^\circ - oq = 90^\circ - 52^\circ 33' = 37^\circ 27'$ .

The only measurement obtained of  $oq$  was  $52^\circ 30'$ , which is adequately near for purposes of confirmation;  $ao$  could not be measured on account of the absence of  $a$ -faces; its double  $oao$  could not be measured either, as only one  $o$ -face was developed. This is, consequently, a case where the calculations are imperatively necessary.

To find  $ao' = (100) : (112)$  and  $ao'' = (100) : (113)$ .

These angles corresponding to the other two kinds of arc-zones terminating at the  $a$ -poles can be similarly found from the two right-angled triangles  $a = (100)$ ,  $o' = (112)$ ,  $p = (110)$ , and  $a = (100)$ ,  $o'' = (113)$ ,  $p = (110)$ . From the Napierian diagrams we derive the equations :

$$\cos ao' = \cos 44^\circ 25' \cos 27^\circ 52'; \quad \cos ao'' = \cos 55^\circ 46' \cos 27^\circ 52'.$$

$$ao' = 50^\circ 51'(50\frac{1}{2}'). \quad ao'' = 60^\circ 11'(10\frac{1}{2}').$$

Then :  $o'o' = (112) : (\bar{1}12) = 2(39^\circ 9\frac{1}{2}') = 78^\circ 19'$ ,  
 and  $o''o'' = (113) : (\bar{1}13) = 2(29^\circ 49\frac{1}{2}') = 59^\circ 39'$ .

The mean measured values for  $o'o'$  and  $o''o''$  respectively were  $78^\circ 19'$  and  $59^\circ 39\frac{1}{2}'$  respectively, a most satisfactory agreement;  $ao'$  and  $ao''$  were not themselves measured on account of the absence of  $a$ -faces.

We next tackle the three analogous zones terminating at the  $b$ -poles.

To find  $bo = (010) : (111)$ ,  $bo' = (010) : (112)$ , and  $bo'' = (010) : (113)$ .

These three angles may be found in a similar manner from the three right-angled triangles  $b = (010)$ ,  $p = (110)$ ,  $o = (111)$ ,  $bpo'$  and  $bpo''$ . Taking first the calculation of  $bo$ , from the Napierian diagram we have :

$$\cos bo = \cos op \cos pb = \cos 26^\circ 6' \cos 62^\circ 8'. \quad bo = 65^\circ 11'.$$

The calculation of  $bo'$  and  $bo''$  from the other two triangles  $bpo'$  and  $bpo''$  will be similar, but instead of  $\cos op$  we shall have  $\cos o'p$  and  $\cos o''p$  respectively.

$$\cos bo' = \cos o'p \cos bp = \cos 44^\circ 25' \cos 62^\circ 8'. \quad bo' = 70^\circ 30'.$$

$$\cos bo'' = \cos o''p \cos bp = \cos 55^\circ 46' \cos 62^\circ 8'. \quad bo'' = 74^\circ 45'.$$

The angles  $oo = (111) : (1\bar{1}1)$ ,  $o'o' = (112) : (1\bar{1}2)$ , and  $o''o'' = (113) : (1\bar{1}3)$  are then each in turn given by the difference between  $180^\circ$  and twice the angles just given :

$$\begin{aligned} oo &= 180^\circ - 2bo = 180^\circ - 130^\circ 22' = 49^\circ 38'; \\ o'o' &= 180^\circ - 2bo' = 180^\circ - 141^\circ 0' = 39^\circ 0'; \\ o''o'' &= 180^\circ - 2bo'' = 180^\circ - 149^\circ 30' = 30^\circ 30'. \end{aligned}$$

In the last of these three zones, between the faces  $b$  and  $o''$ , we meet with a face of the form  $x = \{123\}$ , so that to complete the zone we must now calculate the position of  $x$ .

**To find  $bx = (010) : (123)$  and  $xo'' = (123) : (113)$ .**

This we can do from the anharmonic ratio of the four poles in the  $90^\circ$ -zone [ $b = (010)$ ,  $x = (123)$ ,  $o'' = (113)$ , and  $M = (103)$ ], the latter pole  $M$  being that of a possible but undeveloped face at the intersection of this zone and the zone  $[ac]$ . From the conditions we can immediately set down :

$$\begin{array}{ccc} & 010 & 103 \\ & \times & \times \\ \frac{\sin bx}{\sin bo''} \cdot \frac{\sin Mo''}{\sin Mx} &= \frac{123}{010} \cdot \frac{113}{103}, \\ & \times & \times \\ & 113 & 123 \\ \frac{\sin bx}{\cos bx} \cdot \frac{\cos bo''}{\sin bo''} &= \frac{1}{1} \cdot \frac{1}{2}, \end{array}$$

$$\tan bx = \frac{1}{2} \tan bo'', \text{ that is : } \tan bx = \frac{1}{2} \tan 74^\circ 45'. \quad bx = 61^\circ 25'$$

$$\text{Then : } \quad xo'' = bo'' - bx = 74^\circ 45' - 61^\circ 25' = 13^\circ 20'.$$

The mean measured value of  $o'o'$  was  $39^\circ 1'$ , and of  $o''o''$   $30^\circ 29'$ , the maximum difference of the individual values from the calculated being  $3'$ . The angle  $oo$  could not be measured, as there was only one  $o$ -face developed. The single measured value of  $xo''$  was  $13^\circ 21'$ , only  $1'$  removed from the calculated value.

We are now in a position to find  $cx = (001) : (123)$  and  $p'x = (120) : (123)$ , the angles in the diametral zone  $[cxp']$ . For in the triangle  $b = (010)$ ,  $c = (001)$ ,  $x = (123)$ , we know that  $bc$  is a right angle, that the angle at  $c$  is the angle  $bp' = 43^\circ 24'$ , and that the angle  $bx$  (just found) is  $61^\circ 25'$ .

Constructing the Napierian diagram, we derive from it :

$$\cos 61^\circ 25' = \sin cx \cos 43^\circ 24' \text{ or } \sin cx = \frac{\cos 61^\circ 25'}{\cos 43^\circ 24'}$$

$$cx = 41^\circ 12'.$$

Then, by difference from  $90^\circ$ ,

$$p'x = 48^\circ 48'.$$

The single measurements of these two angles, afforded by the one developed  $x$ -face, were  $41^\circ 15'$  and  $48^\circ 45'$ .

We have still three secondary arc-zones to calculate, in order to obtain a complete survey of the angles on the crystal, namely, two zones with circular arcs ending at the  $p$ -poles, and one such zone with arcs ending at the  $p'$ -poles. The angles in all three zones were measured.

*Angles in the Zone  $[pqxo'p]$ .*

**To find  $pq = (110) : (011)$ .**

This is a simple calculation from the right-angled triangle  $b = (010)$ ,  $q = (011)$ ,  $p = (110)$ , in which we know  $bq = 46^\circ 21'$  and  $bp = 62^\circ 8'$ , both directly from the two basal angles. From the diagram we get by Napier's rules :

$$\cos pq = \cos 46^\circ 21' \cos 62^\circ 8'. \quad pq = 71^\circ 11'.$$

This is identical with the mean measured value of  $pq$ , the individual values only showing a variation of  $1'$  on each side of it.

**To find  $po' = (1\bar{1}0) : (112)$ .**

We can find this angle from the right-angled triangle  $p = (1\bar{1}0)$ ,  $o' = (112)$ ,  $p = (110)$ , in which we know  $pp = 55^\circ 44'$  (basal angle), and  $o'p = 44^\circ 25'$ . From the Napierian diagram we get :

$$\cos po' = \cos 44^\circ 25' \cos 55^\circ 44'. \quad po' = 66^\circ 17'.$$

The mean of the four measured values was  $66^{\circ} 18'$ .

To find  $qx = (011) : (123)$ .

We are obliged here to have recourse to an oblique-angled triangle,  $c = (001)$ ,  $q = (011)$ ,  $x = (123)$ , in which we know the two sides  $cq = 43^{\circ} 39'$  and  $cx = 41^{\circ} 12'$ , and the included angle at  $c$ , which is the angle  $bp' = 43^{\circ} 24'$ . Employing the formulæ for the calculation of the third side given on page 109 of Chapter VII., we have :

$$\tan \theta = \tan 41^{\circ} 12' \cos 43^{\circ} 24'; \quad \cos qx = \frac{\cos 41^{\circ} 12' \cos (43^{\circ} 39' - \theta)}{\cos \theta}.$$

$$\theta = 32^{\circ} 28'.$$

$$qx = 28^{\circ} 59'.$$

$$\text{Then :} \quad xo' = (123) : (112) = 180^{\circ} - (po' + qx + qp) = 180^{\circ} - 166^{\circ} 27' = 13^{\circ} 33'.$$

The single measured values of  $qx$  and  $xo'$  were respectively  $29^{\circ} 0'$  and  $13^{\circ} 34'$ .

*Angles in the Zone [poq'p].*

To find  $po = (1\bar{1}0) : (111)$ ,  $oq' = (111) : (021)$ , and  $q'p = (021) : (1\bar{1}0)$ .

The first and third of these angles may be readily found from the two right-angled triangles  $p = (1\bar{1}0)$ ,  $o = (111)$ ,  $p = (110)$ , and  $b = (010)$ ,  $q' = (021)$ ,  $p = (1\bar{1}0)$ ; constructing the Napierian diagrams we derive therefrom :

$$\cos po = \cos 26^{\circ} 6' \cos 55^{\circ} 44';$$

$$\cos q'p = \cos 27^{\circ} 40' \cos 62^{\circ} 8'.$$

$$po = 59^{\circ} 38'.$$

$$q'p = 65^{\circ} 33'.$$

$$\text{Then :} \quad oq' = 180^{\circ} - (59^{\circ} 38' + 65^{\circ} 33') = 180^{\circ} - 125^{\circ} 11' = 54^{\circ} 49'.$$

The three measured angles were respectively  $59^{\circ} 40'$ ,  $65^{\circ} 33'$ , and  $54^{\circ} 47'$ .

*Angles in the Zone [p'q'o'op'].*

To find  $p'q = (120) : (011)$ .

For this we employ the right-angled triangle  $b = (010)$ ,  $q = (011)$ ,  $p' = (120)$ , in which it is known that the sides  $bq$  and  $bp'$  are respectively  $46^{\circ} 21'$  and  $43^{\circ} 24'$ . From the Napierian diagram we get :

$$\cos p'q = \cos 46^{\circ} 21' \cos 43^{\circ} 24'. \quad p'q = 59^{\circ} 54'.$$

To find  $p'o = (120) : (111)$ .

This is a side of the right-angled triangle  $p' = (120)$ ,  $o = (111)$ ,  $p = (110)$ , in which  $po$  and  $pp'$  are known to be  $26^{\circ} 6'$  and  $18^{\circ} 44'$ , and from the Napierian diagram we derive :

$$\cos p'o = \cos 18^{\circ} 44' \cos 26^{\circ} 6'. \quad p'o = 31^{\circ} 44'.$$

To find  $oo'' = (111) : (1\bar{1}3)$ .

We can find this angle from the oblique triangle  $o = (111)$ ,  $c = (001)$ ,  $o'' = (1\bar{1}3)$ , in which we know the two sides  $co'' = 34^{\circ} 14'$  and  $co = 63^{\circ} 54'$ , as well as the included angle at  $c$ , for this latter is  $p = (110) : p = (1\bar{1}0) = 55^{\circ} 44'$ , one of the basal angles. Employing the formulæ (b) of page 109, Chapter VII., we have :

$$\tan \theta = \tan 34^{\circ} 14' \cos 55^{\circ} 44'; \quad \cos oo'' = \frac{\cos 34^{\circ} 14' \cos (63^{\circ} 54' - \theta)}{\cos \theta}.$$

$$\theta = 20^{\circ} 58'.$$

$$oo'' = 49^{\circ} 35'.$$

$$\text{Then :} \quad o''q = (1\bar{1}3) : (0\bar{1}1) = 180^{\circ} - (p'q + p'o + oo'') = 180^{\circ} - 141^{\circ} 13' = 38^{\circ} 47'.$$

The measured values of these four angles were  $59^{\circ} 54'$  (identical with the calculated),  $31^{\circ} 46'$  ( $2'$  different),  $49^{\circ} 32'$  ( $3'$  different), and  $38^{\circ} 48'$  ( $1'$  different from the calculated), an agreement as satisfactory as can be expected in the case of angles only once measured, there being but one  $o = \{111\}$  face on the crystal.

This completes the whole of the calculations for the crystal of topaz. With only two exceptions, they have been achieved entirely with the



aid of the anharmonic ratio of four poles in a simple  $90^\circ$ -zone, and of Napier's rules for right-angled triangles. In the two exceptional cases only has it been necessary to have recourse to oblique triangles, and then in both cases the calculation has been of the simplest kind, that for which the formulæ were given at (b) on page 109 of Chapter VII.

It now only remains to tabulate the results for topaz in concise form, according to the general scheme set forth at the conclusion of Chapter VIII.

*Table of Results for Crystal of Topaz  $(AlF)_2SiO_4$ .*

**Crystal-System:** Orthorhombic. Class: 8, rhombic holohedral.

**Habit:** Short prismatic.

**Ratio of axes:**  $a : b : c = 0.5287 : 1 : 0.9539$ .

**Forms observed:**  $c = \{001\}$ ,  $p = \{110\}$ ,  $p' = \{120\}$ ,  $q = \{011\}$ ,  $q' = \{021\}$ ,  $o = \{111\}$ ,  $o' = \{112\}$ ,  $o'' = \{113\}$ ,  $x = \{123\}$ .

**Table of interfacial angles:** In the following table the two basal angles are marked with an asterisk:

MORPHOLOGICAL ANGLES OF TOPAZ.

Angle.	No. of Measurements.	Limits.	Mean observed.	Calculated.	Difference.
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp = (110) : (\bar{1}10) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \\ p'p' = (120) : (\bar{1}20) \end{array} \right.$	$\begin{array}{c} \dots \\ 2 \\ 4 \\ \dots \\ 2 \end{array}$	$\begin{array}{c} \circ \quad ' \quad \circ \quad ' \\ \dots \\ 55 \quad 43-55 \quad 45 \\ 18 \quad 42-18 \quad 47 \\ \dots \\ 86 \quad 46-86 \quad 50 \end{array}$	$\begin{array}{c} \circ \quad ' \\ \dots \\ 55 \quad 44 \\ 18 \quad 44 \\ \dots \\ 86 \quad 48 \end{array}$	$\begin{array}{c} \circ \quad ' \\ 27 \quad 52 \\ * \\ 18 \quad 44 \\ 43 \quad 24 \\ 86 \quad 48 \end{array}$	$\begin{array}{c} ' \\ \dots \\ \dots \\ 0 \\ \dots \\ 0 \end{array}$
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qq' = (011) : (021) \\ q'b = (021) : (010) \\ cq' = (001) : (021) \end{array} \right.$	$\begin{array}{c} 2 \\ 2 \\ \dots \\ 2 \end{array}$	$\begin{array}{c} 43 \quad 39-43 \quad 39 \\ 18 \quad 39-18 \quad 41 \\ \dots \\ 62 \quad 18-62 \quad 20 \end{array}$	$\begin{array}{c} 43 \quad 39 \\ 18 \quad 40 \\ \dots \\ 62 \quad 19 \end{array}$	$\begin{array}{c} * \\ 18 \quad 41 \\ 27 \quad 40 \\ 62 \quad 20 \end{array}$	$\begin{array}{c} \dots \\ 1 \\ \dots \\ 1 \end{array}$
$\left\{ \begin{array}{l} co'' = (001) : (113) \\ o''o' = (113) : (112) \\ o'o = (112) : (111) \\ co = (001) : (111) \\ co' = (001) : (112) \\ op = (111) : (110) \\ o'p = (112) : (110) \end{array} \right.$	$\begin{array}{c} 4 \\ 4 \\ 1 \\ 1 \\ 4 \\ 1 \\ 4 \end{array}$	$\begin{array}{c} 34 \quad 13-34 \quad 16 \\ 11 \quad 19-11 \quad 21 \\ \dots \\ \dots \\ 45 \quad 32-45 \quad 36 \\ \dots \\ 44 \quad 24-44 \quad 25 \end{array}$	$\begin{array}{c} 34 \quad 14 \\ 11 \quad 20 \\ 18 \quad 17 \\ 63 \quad 50 \\ 45 \quad 34 \\ 26 \quad 8 \\ 44 \quad 25 \end{array}$	$\begin{array}{c} 34 \quad 14 \\ 11 \quad 21 \\ 18 \quad 19 \\ 63 \quad 54 \\ 45 \quad 35 \\ 26 \quad 6 \\ 44 \quad 25 \end{array}$	$\begin{array}{c} 0 \\ 1 \\ 2 \\ 4 \\ 1 \\ 2 \\ 0 \end{array}$
$\left\{ \begin{array}{l} cx = (001) : (123) \\ xp' = (123) : (120) \end{array} \right.$	$\begin{array}{c} 1 \\ 1 \end{array}$	$\begin{array}{c} \dots \\ \dots \end{array}$	$\begin{array}{c} 41 \quad 15 \\ 48 \quad 45 \end{array}$	$\begin{array}{c} 41 \quad 12 \\ 48 \quad 48 \end{array}$	$\begin{array}{c} 3 \\ 3 \end{array}$
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \end{array} \right.$	$\begin{array}{c} \dots \\ 1 \end{array}$	$\begin{array}{c} \dots \\ \dots \end{array}$	$\begin{array}{c} \dots \\ 52 \quad 30 \end{array}$	$\begin{array}{c} 37 \quad 27 \\ 52 \quad 33 \end{array}$	$\begin{array}{c} \dots \\ 3 \end{array}$
$\left\{ \begin{array}{l} ao' = (100) : (112) \\ o'o' = (112) : (\bar{1}12) \end{array} \right.$	$\begin{array}{c} \dots \\ 2 \end{array}$	$\begin{array}{c} \dots \\ 78 \quad 18-78 \quad 20 \end{array}$	$\begin{array}{c} \dots \\ 78 \quad 19 \end{array}$	$\begin{array}{c} 50 \quad 51 \\ 78 \quad 19 \end{array}$	$\begin{array}{c} \dots \\ 0 \end{array}$
$\left\{ \begin{array}{l} ao'' = (100) : (113) \\ o''o'' = (113) : (\bar{1}13) \end{array} \right.$	$\begin{array}{c} \dots \\ 2 \end{array}$	$\begin{array}{c} \dots \\ 59 \quad 37-59 \quad 42 \end{array}$	$\begin{array}{c} \dots \\ 59 \quad 39 \end{array}$	$\begin{array}{c} 60 \quad 11 \\ 59 \quad 39 \end{array}$	$\begin{array}{c} \dots \\ 0 \end{array}$
$\left\{ \begin{array}{l} bo = (010) : (111) \\ oo = (111) : (\bar{1}11) \end{array} \right.$	$\begin{array}{c} \dots \\ \dots \end{array}$	$\begin{array}{c} \dots \\ \dots \end{array}$	$\begin{array}{c} \dots \\ \dots \end{array}$	$\begin{array}{c} 65 \quad 11 \\ 49 \quad 38 \end{array}$	$\begin{array}{c} \dots \\ \dots \end{array}$

MORPHOLOGICAL ANGLES OF TOPAZ (*Continued*).

Angle.	No. of Measurements.	Limits.	Mean observed.	Calculated.	Difference.
$\left\{ \begin{array}{l} bo' = (010) : (112) \\ o'o' = (112) : (\bar{1}\bar{1}2) \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} \circ \quad ' \quad \circ \quad ' \\ 39 \quad 0-39 \quad 3 \end{array} \right.$	$\left\{ \begin{array}{l} \circ \quad \dots \quad ' \\ 39 \quad 1 \end{array} \right.$	$\left\{ \begin{array}{l} 70 \quad 30 \\ 39 \quad 0 \end{array} \right.$	$\left\{ \begin{array}{l} ' \\ \dots \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} bx = (010) : (123) \\ xo'' = (123) : (113) \\ bo'' = (010) : (113) \\ o''o'' = (113) : (\bar{1}\bar{1}3) \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ 1 \\ \dots \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ \dots \\ \dots \\ 30 \quad 29-30 \quad 29 \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ 13 \quad 21 \\ \dots \\ 30 \quad 29 \end{array} \right.$	$\left\{ \begin{array}{l} 61 \quad 25 \\ 13 \quad 20 \\ 74 \quad 45 \\ 30 \quad 30 \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ 1 \\ \dots \\ 1 \end{array} \right.$
$\left\{ \begin{array}{l} po' = (1\bar{1}0) : (112) \\ o'x = (112) : (123) \\ xq = (123) : (011) \\ o'q = (112) : (011) \\ qp = (011) : (\bar{1}\bar{1}0) \end{array} \right.$	$\left\{ \begin{array}{l} 4 \\ 1 \\ 1 \\ 4 \\ 4 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \quad 14-66 \quad 20 \\ \dots \\ \dots \\ 42 \quad 29-42 \quad 34 \\ 71 \quad 10-71 \quad 12 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \quad 18 \\ 13 \quad 34 \\ 29 \quad 0 \\ 42 \quad 31 \\ 71 \quad 11 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \quad 17 \\ 13 \quad 33 \\ 28 \quad 59 \\ 42 \quad 32 \\ 71 \quad 11 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \\ 1 \\ 1 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} po = (1\bar{1}0) : (111) \\ oq' = (111) : (021) \\ q'p = (021) : (\bar{1}\bar{1}0) \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ \dots \\ \dots \end{array} \right.$	$\left\{ \begin{array}{l} 59 \quad 40 \\ 54 \quad 47 \\ 65 \quad 33 \end{array} \right.$	$\left\{ \begin{array}{l} 59 \quad 38 \\ 54 \quad 49 \\ 65 \quad 33 \end{array} \right.$	$\left\{ \begin{array}{l} 2 \\ 2 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} p'o = (120) : (111) \\ oo'' = (111) : (\bar{1}\bar{1}3) \\ o''q = (\bar{1}\bar{1}3) : (011) \\ qp' = (011) : (\bar{1}\bar{2}0) \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \\ 1 \\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} \dots \\ \dots \\ \dots \\ \dots \end{array} \right.$	$\left\{ \begin{array}{l} 31 \quad 46 \\ 49 \quad 32 \\ 38 \quad 48 \\ 59 \quad 54 \end{array} \right.$	$\left\{ \begin{array}{l} 31 \quad 44 \\ 49 \quad 35 \\ 38 \quad 47 \\ 59 \quad 54 \end{array} \right.$	$\left\{ \begin{array}{l} 2 \\ 3 \\ 1 \\ 0 \end{array} \right.$

The general agreement between the observed and calculated angles is obviously of a satisfactory character.

It has already been remarked that there is an alternative choice of parametral plane possible, to the one due to von Kokscharow made in the preceding description. The parametral form  $o = \{111\}$  has been shown to have been only represented by a single face on the crystal under consideration, and it appears in general to be less developed on crystals of topaz than the form  $o' = \{112\}$ . Owing, therefore, to the apparent greater importance of the form  $o'$ , and to the fact that the cleavage does not help us to decide between the merits of the two forms as possible parametral planes, or at any rate does not make the choice of  $o = \{111\}$  imperative, topaz cleaving parallel to the basal pinakoid  $c = \{001\}$ , Miers, in his *Mineralogy* (page 442) takes  $o'$  as the parametral form  $\{111\}$ . This causes the form  $o''$  to become  $\{223\}$ , and  $o$  to become  $\{221\}$ . That this is so may readily be proved by setting out the anharmonic ratio of either the four poles  $c = (001)$ ,  $o'' = (hhl)$ ,  $o' = (111)$ , and  $p = (110)$ , or  $c = (001)$ ,  $o' = (111)$ ,  $o = (hhl)$ , and  $p = (110)$ , in the  $90^\circ$ -arc  $cp$ , giving the angles their measured values while  $o''$  and  $o$  are represented by  $(hhl)$ . It will be found that in the two cases the ratio works out to give values for  $h$  and  $l$  as follows :

$$\tan 44^\circ 25' \cdot \tan 34^\circ 14' = h/l, \text{ and } \tan 26^\circ 6' \cdot \tan 45^\circ 35' = l/h.$$

The numerical value of the first is 0.6667, or  $2/3$ , and of the second 0.500 or  $1/2$ . Hence  $(hhl)$  in the first case (that of the face  $o''$ ) is  $(223)$ , and in the second case (that of the face  $o$ )  $(hhl) = (221)$ . The two forms in the zone  $[cb]$ , namely,  $q$  and  $q'$ , become respectively  $\{021\}$  and  $\{041\}$ . The former is given at once by cross-multiplication of the zones  $[a = (100) : o = (221)]$  and  $[c = (001) : b = (010)]$ , as  $q$  is at the intersection of these two zones; and the latter can then be found by considering the pole  $q'$  as the fourth in the  $90^\circ$ -zone  $[c = (001)$ ,  $q = (021)$ ,  $b = (010)]$  and setting out the anharmonic

ratio, giving the angles their measured values and calling the indices  $(0kl)$ . The ratio then works out to :

$$\tan 27^\circ 40' \tan 43^\circ 39' = 2l/k.$$

The numerical value of the product of the two tangents is 0.50, so that

$$\frac{2l}{k} = \frac{1}{2}, \text{ and } k = 4l.$$

The indices of  $q'$  are, therefore  $\{041\}$ , for the face is parallel to the axis  $a$ , so that the value of  $h$  is 0.

The effect of thus taking  $o'$  as the parametral plane (111) instead of  $o$ , on the ratio of the axes is to diminish the length of the  $c$  axis by one half relatively to that of the  $b$  axis, thus making it 0.477, the value of  $a/b$  remaining unaltered. For the length of axis which is given by  $\tan cq$ , the expression for  $c/b$ , is now  $2c$  instead of  $c$ . The actual values of the axial ratios given by Miers are :

$$a : b : c = 0.528 : 1 : 0.477.$$

This instance of the possibility of two alternative courses, as regards the choice of the parametral plane defining the axial lengths and determining the indices of faces other than the axial planes, is a very typical one. The question of the proper "setting up" of a crystal, that is, as to which axis shall be vertical, which lateral, and which shall run back-and-front, and of the correct choice of the parametral plane, is a very important one, but as yet somewhat obscure. That it has a profound bearing on the correct diagnosis of the internal structure will be obvious, and a subsequent chapter (XXXIV). will be devoted to discussing it, and to the description of a method for its elucidation which has been proposed and found very successful by E. S. Fedorov. In the case of topaz in all probability the "setting up" here adopted is the proper one both on von Kokscharow's assumption and on that of Miers, but as to which choice of parametral plane is correct there is as yet no decisive evidence to show, that of cleavage, often of great importance, being here inoperative.



## CHAPTER XVI

### MONOCLINIC SYSTEM

*Also called Monosymmetric and Oblique System.*

Three unequal crystallographic axes, of which one is perpendicular to the other two.

Characterised by possessing either a digonal axis and a plane of symmetry perpendicular to it, or only one of these elements.

THERE are obviously three classes fulfilling these conditions, namely: one, class 3, possessing only a plane of symmetry; a second, class 4, having only a digonal axis; and a third, class 5, possessing both a digonal



FIG. 199.—Symmetry Element and General Form of Class 3.

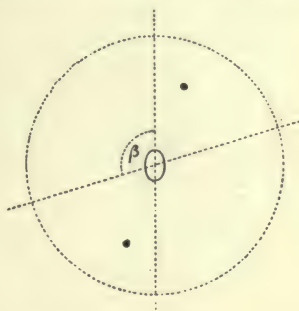


FIG. 200.—Symmetry Element and General Form of Class 4.

axis and a plane of symmetry at right angles to it. These three classes are respectively illustrated by the stereographic projections given in Figs. 199, 200, and 201. The plane of symmetry of classes 3 and 5 is taken as the plane of projection, that of the paper, and is represented by the primitive circle being drawn in continuous line, as distinguished from the dotted circle of class 4, Fig. 200. The digonal axis is perpendicular to this plane, and its projection is consequently the centre of the circle. The two dotted straight lines represent the vertical and inclined crystallographic axes, lying in the plane of possible symmetry and inclined to

each other at the axial angle  $\beta$ . The third crystallographic axis perpendicular to these two is identical with the digonal axis of symmetry.

*Class 5.—Monoclinic-Prismatic Class. Monoclinic-Holohedral Class.  
Type, Digonal Equatorial.*

This holohedral class of the monoclinic system possesses, as its name holohedral implies, both the elements of symmetry referred to on page 247. They are graphically expressed in the stereographic projection given in Fig. 201, which also shows not only the poles of the primary representative  $\{11\bar{1}\}$  of the most general form  $\{hkl\}$ , but also those of the primary pinakoidal forms  $\{100\}$ ,  $\{010\}$ , and  $\{001\}$ , together with the section-outline of the actual faces of the forms  $\{100\}$  and  $\{001\}$  made by the symmetry plane  $\{010\}$ . It will be observed that a different mode of projection is adopted from that which has been employed in connection with the other systems, the great circle bearing the poles of the faces  $(100)$  and  $(001)$  parallel to the two crystallographic axial planes  $bc$  and  $ab$ , and which in fact have been themselves chosen for those axial planes, being the primitive circle instead of that bearing  $(100)$  and  $(010)$ . The reason is one of very great convenience, for the axis  $b$ , perpendicular to the other two axes, which is the one symmetry axis and is chosen as  $b$  axis because it is so, is thereby brought per-

pendicular to the plane of the paper; and the latter plane, represented by the primitive circle, is the one symmetry plane of the system, in which lie the other two axes  $a$  and  $c$ , which may have any mutual inclination, other than  $90^\circ$ , to each other in that plane. The symmetry is thus at once shown by such a mode of projection, and pairs of faces symmetrical to the symmetry plane may be represented by a dot and concentric ring as usual.

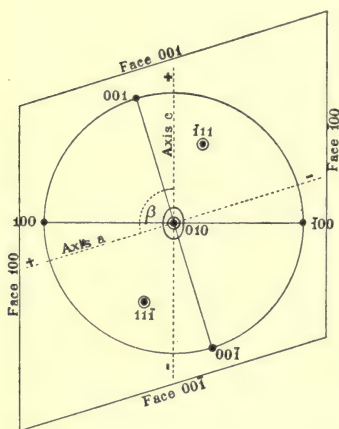


FIG. 201.—Symmetry Elements, Axial Planes, and General Form of Class 5.

The digonal axis, identical, as above stated, with the crystallographic axis  $b$ , is represented by the pole in the centre, which also indicates the position of the faces  $(010)$  and  $(0\bar{1}0)$ , the symmetry plane being, in fact, the plane  $\{010\}$ . A horizontal diameter is then drawn,

and the pole of the face  $(100)$  is placed at the left end of it, its parallel face  $(\bar{1}00)$  being represented by a pole at the right end. The pole of the face  $(001)$  is then inserted at the proper position on the primitive circle, so that the angle between the normal to  $(100)$ , represented by the horizontal diameter, and the normal to the face  $(001)$ , which may be represented by another diameter, is the actual angle measured on the goniometer between the faces  $(100)$  and  $(001)$ . This acute angle

(100):(001), represented by the acute angle between the diameters, is the supplement of the crystallographic axial angle  $\beta$ , between the two inclined axes,  $a$  and  $c$ , for the axis  $a$  is parallel to the edge (010):(001), and the axis  $c$  is parallel to the edge (010):(100), these edges having been chosen deliberately as such axes. The edge (100):(001) is similarly the chosen direction of the symmetry axis  $b$ , and is perpendicular to the  $a$  and  $c$  axes (the two edges just referred to) and to the symmetry plane containing them. This arrangement brings the  $c$  axis vertical, as is desirable for reasons of analogy with the more symmetrical systems. The monoclinic differs from these higher systems by the inclination of the  $a$  axis, which is tilted downwards towards the left in the projection, as will be clear from the dotted lines indicating these two axes  $a$  and  $c$  lying in the symmetry plane.

It must be clearly pointed out, however, that this arrangement is only for the purposes of the stereographic projection. For descriptive purposes and pictorial representation the  $a$  axis is, as usual, the back-to-front axis, and in this system tilts downwards towards the observer when the crystal is held in position, the axis  $c$  being vertical and the symmetry axis  $b$  running horizontally right-and-left. The crystal is thus rotated  $90^\circ$  round the vertical axis for the purpose of projection, in order to bring the symmetry plane into coincidence with the plane of the paper.

It must also be clearly understood that the poles (100) and (001) do not lie on the  $a$  and  $c$  axes, as is usual in the rectangular systems, but that the vertical axis is parallel to the tangent to the circle at the pole (100), that is, parallel to the face represented by the pole, and the inclined  $a$  axis is parallel to the tangent at the pole (001), or to the face represented by that pole.

As regards the axial angle  $\beta$ , the only one of the three axial angles which is not  $90^\circ$ , it is equally well expressed either by the actually measured goniometrical angle (100):(001) or by the supplement of that angle already referred to; for the former is equal to the acute angle between the inclined axes, and the latter to the obtuse angle. The obtuse angle is the actual angle between the two primary edges above quoted, and is also the angle in the positive part of the upper hemisphere, and so it has in the past been generally given as the angle  $\beta$ ; as this angle is obviously greater than  $90^\circ$ , it has, however, been recently coming into practice to give instead the acute angle as the value of  $\beta$ , as measured directly, between the normals to the faces (100) and (001), on the goniometer.

The symmetry axis  $b$ , being at right angles to the vertical axis, is termed the "ortho-diagonal" for descriptive purposes, and the axis  $a$  because inclined to the vertical axis  $c$ , is called the "clino-diagonal."

The pair of faces (100) and ( $\bar{1}00$ ), the poles of which are situated at the end of the horizontal diameter in the projection, are a form unto themselves in this system, and being parallel to the ortho-diagonal as well as to the vertical axis the form is termed the **ortho-pinakoid**, its symbol being {100}.

Similarly, the pair of faces (010) and (0 $\bar{1}$ 0), the poles of which lie over each other



at the centre (as a dot with concentric ring if it be desired to represent both), and which are parallel to the clino-diagonal and the vertical axis as well as being the facial expression of the symmetry plane itself, also together make up a separate form  $\{010\}$  distinguished by the name **clino-pinakoid**.

Likewise the basal plane  $(001)$  and its parallel face  $(00\bar{1})$ , both of which are parallel to the inclined axis (clino-diagonal) and the symmetry axis (ortho-diagonal), together make up a third primary form of pinakoidal character,  $\{001\}$ , which may be termed the **basal-pinakoid**.

These three fundamental forms in combination produce the closed prism-like solid

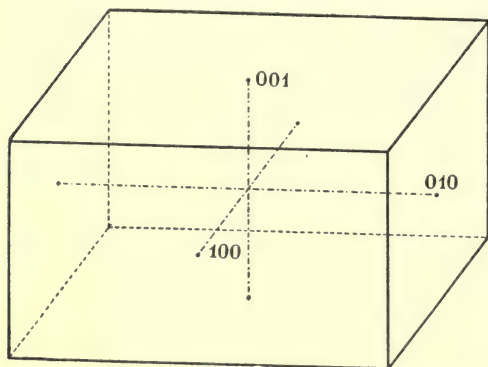


FIG. 202.—Combination of the three Primary Monoclinic Pinakoids forming Oblique Rectangular Prism.

shown in Fig. 202, formerly known as "the oblique rectangular prism," which is the monoclinic equivalent of the cube, or of the tetragonal prism of the second order or the rectangular rhombic prism, but with the horizontal pair of faces tilted downwards towards the observer. The two pairs of faces of the ortho- and basal pinakoids are rectangular in shape, but the pair of clino-pinakoids are parallelograms the opposite pairs of equal angles of which are equal respectively to the crystallographic axial angle  $\beta$  and to its supplement.

These three forms will have been chosen, at the commencement of the investigation of the crystal, as the axial planes, and their edges of intersection as the directions of the three crystallographic axes.

The general form  $\{hkl\}$ , of which the primary parametral form  $\{111\}$  (which will have been chosen to determine the lengths of the three crystallographic axes) is a special case, consists of four faces, as will be clear from the stereographic projection given in Fig. 201, namely,  $(hkl)$ ,  $(\bar{h}\bar{k}\bar{l})$ ,  $(\bar{h}kl)$ , and  $(h\bar{k}\bar{l})$ ; they together make up an open prism-like form of rhombic section, of which one of the two diagonals lies in the symmetry plane, but in combination with the complementary form  $\{hk\bar{l}\}$ , the actual one shown in Fig. 201, a monoclinic bipyramid is produced. Each of the two forms  $\{hkl\}$  and  $\{hk\bar{l}\}$  is therefore commonly designated as a **monoclinic hemi-pyramid**. It is termed a prism of the fourth order by von Groth and Fedorov, because it is not parallel to any one of the three axes; and it is this general, or fourth order, prism which gives the name "prismatic" to the class. A monoclinic bipyramid thus composed of the two complementary hemi-pyramids or fourth order prisms is shown in Fig. 203, which represents it considered as the primary one. The four faces of the first form,  $\{hkl\}$ , situated in the obtuse angles of the inclined axes, two faces vertically over each other in the projection in each case, are usually referred to as forming the **negative hemi-pyramid** or negative fourth order prism (negative because the poles are situated in the obtuse axial angle  $\beta$ ); while the form  $\{hk\bar{l}\}$  shown in the projection, Fig. 201, with poles in the acute axial angles, is regarded as the **positive hemi-pyramid** or positive prism of the fourth order (positive because the poles are in the acute axial angle).

Thus in the monoclinic system, for the first time (taking the systems as we are doing, in descending order), we have the holohedral pyramidal solid (the bipyramid) divided into two separate forms. In the case of the parametral bipyramid, shown in Fig. 203, we have the two forms  $\{111\}$  and  $\{1\bar{1}\bar{1}\}$ .

There are three further types of forms, corresponding to special cases of the general form  $\{hkl\}$ , afforded when the latter migrates on to one of the sides of the fundamental spherical triangle (Fig. 201) formed by the poles (100), (010), and (001). In each case the faces of the form produced are parallel to one or other of the three crystallographic axes, and are therefore respectively said to be of the "first," "second," or "third" order by von Groth and Fedorov.

In the first case, when the pole lies on the side (100):(010), the symmetry conditions demand that there shall be four faces in the form; one pole is situated immediately beneath the first pole, on the lower hemisphere, owing to the presence of the symmetry plane, and a similar pair are situated above and below each other on

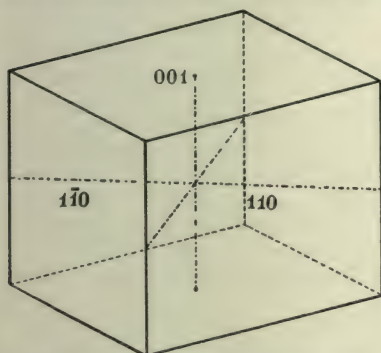


FIG. 204.—The Primary Monoclinic Prism with Basal Pinakoid.

migrates on to the arc (010):(001), a similar four-faced open prism is produced, likewise symmetrical to the symmetry plane and to the centre, but the faces and edges of which are parallel to the clino-diagonal, the axis  $a$ . It is, therefore, a prism of the first order, and is generally termed a **clino-prism** or **clino-domal prism**, and has the general symbol  $\{0kl\}$ , the primary clino-prism being  $\{011\}$ . The latter is shown in Fig. 205, in combination with and closed by the ortho-pinakoid  $\{100\}$ .

The third case is when the pole has migrated to the side (100):(001), that is, on to the primitive circle, and therefore lies in the plane of symmetry;

the symmetry axis is thus parallel to the faces and edges of all such forms, being their zone axis, and the zone will include also the faces of the ortho-pinakoid and of the basal

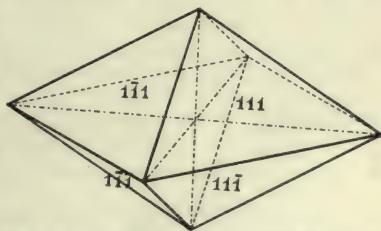


FIG. 203.—The Primary Monoclinic Bipyramid (2 Forms).

the same horizontal-diametral arc at the other side of the centre, owing to the operation of the digonal symmetry axis. These four faces, opposite pairs of which are parallel, thus form an open prism of rhombic section, all the faces and edges of which are parallel to the vertical axis  $c$ , and the prism is therefore of the third order according to the Groth-Fedorov classification. It is generally termed a **monoclinic prism**, and the symbol of the most general form is  $\{hk0\}$  and that of the primary prism  $\{110\}$ . The latter is shown in Fig 204 in combination with and closed by its most fundamental termination, the basal pinakoid  $\{001\}$ .

In the second case, when the pole

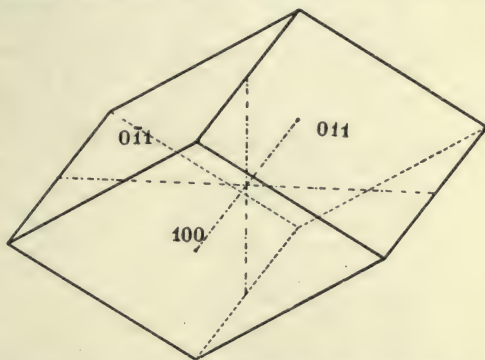


FIG. 205.—The Primary Clinodomal Prism with Ortho-Pinakoid.

pinakoid. Now the operation of the only element of symmetry here able to act, the digonal axis, only requires that any face, the pole of which lies on this primitive zone-circle, should have another face parallel to it. Hence, as in the case of the ortho-pinakoid, the form consists of two faces only, parallel to each other, and the two other complementary faces having similar indices, the poles of which lie in the acute angle of the inclined axes, belong to a separate pinakoidal form, termed the positive, the original form with poles in the obtuse angle being the negative. The two forms together make up an open prism parallel to the ortho-diagonal, the symmetry axis  $b$ , and which is called, analogously to the clino-prism, an ortho-prism or orthodomal prism. Hence the two separate forms are hemi-prisms, or pinakoids

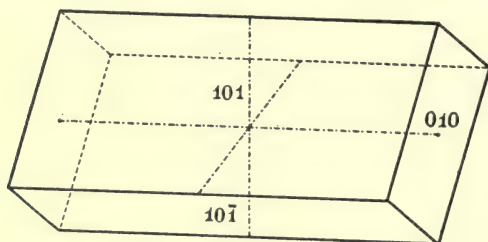


FIG. 206.—Combination of the two Primary Orthodomal Prisms and Clinopinakoid.

of the second order, and are generally known as the **negative hemi-ortho-prism** or **orthodomal prism**  $\{h0\bar{l}\}$ , and the **positive hemi-ortho-prism** or **orthodomal prism**  $\{h0l\}$ . Fig. 206 represents such a combination of two ortho-prisms, in this case the primary ones  $\{101\}$  and  $\{10\bar{1}\}$ , terminated laterally by the clino-pinakoid  $\{010\}$ .

The holohedral class of the monoclinic system comprises, therefore, the forms given in the following list; besides the descriptive name referred to in the foregoing description, each form is also labelled with the name indicative of the character of the form as to whether it is a "first," "second," or "third" pinakoid, or a prism or pinakoid of a particular "order," in accordance with the scheme outlined in connection with the rhombic system (Chapter XIV. p. 226).

*List of Forms in Class 5.*

- $\{001\}$  Basal pinakoid; or third pinakoid. 2 faces.
- $\{100\}$  Ortho-pinakoid; or first pinakoid. 2 faces.
- $\{010\}$  Clino-pinakoid; or second pinakoid. 2 faces.
- $\{hk0\}$  Monoclinic prism, or monoclinic prism of the third order, including the primary prism  $\{110\}$ . 4 faces.
- $\{h0l\}$  Negative hemi-ortho-prism or hemi-orthodomal prism, or monoclinic pinakoid of the second order, including the primary one  $\{101\}$ ;  $\{h0\bar{l}\}$  positive hemi-ortho-prism, or -domal prism, or second order pinakoid, including the primary  $\{10\bar{1}\}$ . Each 2 faces.
- $\{0kl\}$  Clino-prism or clinodomal prism, or monoclinic prism of the first order, including the primary form  $\{011\}$ . 4 faces.
- $\{hkl\}$  Negative monoclinic hemi-pyramid, or prism of the fourth order, including the parametral hemi-pyramid or prism  $\{111\}$ ;  $\{h\bar{k}l\}$  positive monoclinic hemi-pyramid, or fourth order prism, including the complementary primary hemi-pyramid or prism  $\{11\bar{1}\}$ . Each 4 faces.

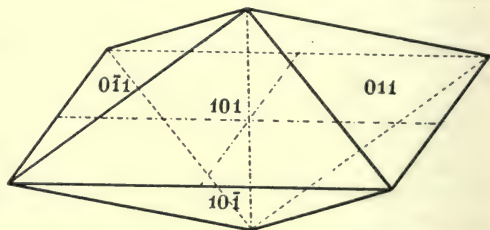


FIG. 207.—Combination of Clino- and Orthodomal Prisms forming Oblique Rectangular Pyramid (3 Forms).

The two last cases but one, the clinodomal prism and the two hemi-orthodomal



prisms, when in combination produce a solid of pyramidal form, which used to be distinguished as the "oblique rectangular pyramid," being comparable to the rectangular rhombic pyramid but with an inclined equatorial plane. Such a combination is shown in Fig. 207, but it very rarely indeed happens that the three forms are present in the exact equipoise shown in the figure. Usually the three are developed to different extents, frequently one or other of them largely preponderating.

Excellent examples of substances crystallising according to holohedral monoclinic symmetry are afforded by the well-known series of isomorphous double sulphates and selenates the generic formula of which is  $R_2M\left(\begin{smallmatrix} S \\ Se \end{smallmatrix} O_4\right)_2 \cdot 6H_2O$ , in which R may be potassium, rubidium, caesium, thallium, or ammonium, and M may be magnesium, zinc, iron, nickel, cobalt, manganese, copper, or cadmium. Sixty-two of these salts have been investigated up to the year 1920 in great detail by the author, and the results published in numerous memoirs; also the collected results up

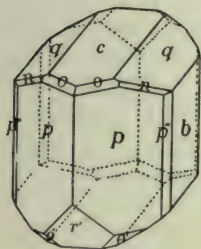


FIG. 208.

Crystal of Ammonium Magnesium Sulphate.

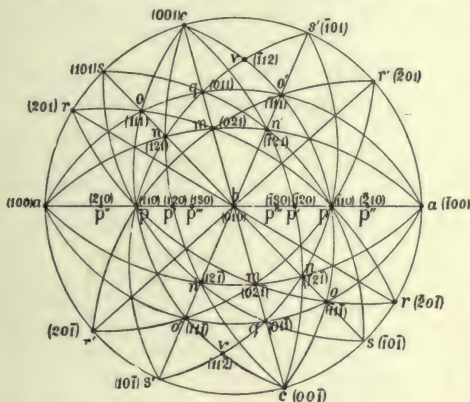


FIG. 209.—Stereographic Projection of Monoclinic Series  
 $R_2M(S_8O_4)_3 \cdot 6H_2O$ .

to the end of the year 1909 were published in book form.<sup>1</sup> One of these salts will be considered in detail in the next chapter, as a practical example of the goniometry of this system, so that it is unnecessary here to refer further to them, except in passing to give an illustration of their general type of combination in Fig. 208, which represents a crystal of ammonium magnesium sulphate, showing as its forms: the clino-pinakoid  $b = \{010\}$ , the basal pinakoid  $c = \{001\}$ , the prisms  $p = \{110\}$  and  $p''' = \{130\}$ , the clino-prism  $q = \{011\}$ , the positive hemi-ortho-prism  $r' = \{201\}$ , the primary hemi-pyramids  $o = \{111\}$  and  $o' = \{\bar{1}11\}$ , and the hemi-pyramid  $n = \{121\}$ . On other salts of the series still more forms are developed, and the general stereographic projection of the series is here given in Fig. 209 (taken from the author's first memoir on the double sulphates<sup>2</sup>) as a practical example of a monoclinic projection showing the poles of the whole of the types of forms enumerated in the list of class 5 forms.

<sup>1</sup> *Crystalline Structure and Chemical Constitution*, Macmillan and Co., Ltd., 1910.

<sup>2</sup> *Journ. Chem. Soc.*, 1893, 63, 343.

The recognition of monoclinic symmetry in a new substance will usually be a fairly simple matter after a few measurements have been made, and the stereographic projection has been constructed. For the plane of symmetry will soon make itself apparent, and the fact that no symmetry is shown along any other plane at right angles to the one recognised as a plane of symmetry, that is, the fact of the absence of other than centro-symmetry among the poles lying in that recognised symmetry plane, will show that the system cannot be orthorhombic, or at any rate cannot be holohedral-orthorhombic, and certainly nothing higher still.

As regards the calculation of the elements, general directions for the case of the monoclinic system have already been given in Chapter VII., and they will be practically employed in the next chapter dealing with the concrete example just referred to.

*Class 4.—Monoclinic-Sphenoidal Class. Monoclinic-Hemimorphic Class. Type, Digonal Polar.*

The symmetry plane is eliminated in this class, and the only element of symmetry present is the digonal axis, as shown in the stereographic projection in Fig. 210, which also gives the positions of the poles of one of the varieties of the general form  $\{hkl\}$ .

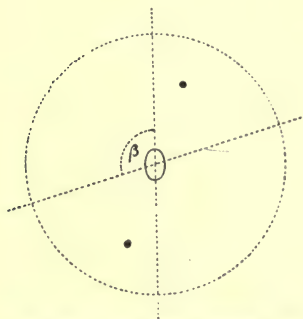


FIG. 210.—Symmetry Element and General Form of Class 4.

It will be at once apparent that the latter consists now of only two faces, both of which are at the same end of the symmetry axis, that is, on the same side of the crystallographic axial plane  $ac$ , which is no longer a plane of symmetry. There will be two modifications of the form at the two different ends of the axis. The pair of faces in the first form have the indices  $(hkl)$  and  $(\bar{h}k\bar{l})$ ; the pair comprising the other enantiomorphous modification will be  $(h\bar{k}l)$  and  $(\bar{h}k\bar{l})$ , hence the form symbols are  $\{hkl\}$  and  $\{h\bar{k}l\}$ , the former being the right variety and the latter the left modification, both negative, because

the poles are situated in the obtuse axial angle  $\beta$ . There will also be two other similar but positive forms, when the poles lie inside the acute instead of the obtuse angles of the axes  $a$  and  $c$ . The right variety will consist of the two faces  $(\bar{h}kl)$  and  $(h\bar{k}l)$ , and its primary representative is the one the poles of which are shown in Fig. 210. The left variety will consist of the pair of faces  $(\bar{h}k\bar{l})$  and  $(h\bar{k}\bar{l})$ . The symbols of the forms will thus be  $\{hkl\}$  and  $\{h\bar{k}l\}$ . The four primary forms will consequently be  $\{111\}$ ,  $\{1\bar{1}1\}$ ,  $\{\bar{1}11\}$ , and  $\{\bar{1}\bar{1}1\}$ . All these forms, general and primary, are termed **monoclinic sphenoids**, from the Greek word  $\sigma\phi\eta\nu$ , meaning "wedge," being pairs of faces forming a wedge in each case, and which, together with the variety of opposite sign at the other end of the symmetry axis in each case, make up a closed so-called "oblique bisphenoid," which is the monoclinic representative of the tetrahedron.

Such sphenoids are of the fourth order according to the Groth-Fedorov classification, as they are not parallel to any one of the three crystallographic axes.

The usual six special cases are obtained when the pole lies on one of the sides of the fundamental spherical triangle formed by the poles  $(100)$ ,  $(010)$ , and  $(001)$  (see

Figs. 201 and 209), or at one of the angles. The same forms result as regards the side  $\{100\} : \{001\}$ , that is, when the poles lie on the primitive circle, as in the holohedral class. As in that class, the ortho-pinakoid (first pinakoid)  $\{100\}$ , basal pinakoid (third pinakoid)  $\{001\}$ , and the hemi-ortho-prism or hemi-orthodomal prism (pinakoid of the second order)  $\{h0l\}$ , each consists of a pair of faces parallel to each other and to the symmetry axis. On the other hand the forms the poles of which lie on the other sides of the triangle, the clino-prisms or domes (first order prisms)  $\{0kl\}$  and the monoclinic prisms (third order prisms)  $\{hkl\}$ , will consist of two faces only, forming a sphenoid of the first or third order, instead of four, the four holohedral faces being divided into two separate pairs, one at each end of the symmetry axis, that is, a right and a left form, the right form having the same symbol as the holohedral form, and the left variety having a negative  $k$  index number.

Moreover, the clino-pinakoid, consisting of two faces parallel to each other and to the symmetry plane in the holohedral class, now divides into two single-face or pedial forms, the right clino-pedion (second pedion)  $\{010\}$  and the left clino-pedion  $\{0\bar{1}0\}$ , employing the term "pedion" proposed by Professor von Groth for such single-face forms.

To summarise, we have the following forms in this class :

*List of Forms in Class 4.*

- $\{001\}$  Basal pinakoid, or third pinakoid. 2 faces.
- $\{100\}$  Ortho-pinakoid, or first pinakoid. 2 faces.
- $\{010\}$  Right clino-pedion, or right second pedion ;  $\{0\bar{1}0\}$  left clino-pedion, or left second pedion. Each 1 face.
- $\{hkl\}$  Right monoclinic prism, or sphenoid of the third order, including the primary prism or sphenoid  $\{110\}$  ;  $\{h\bar{k}l\}$  left form of same, including the primary  $\{1\bar{1}0\}$ . Each 2 faces.
- $\{h0l\}$  Negative hemi-ortho-prism or hemi-orthodomal prism, or negative pinakoid of the second order, including the primary  $\{101\}$  ;  $\{h0\bar{l}\}$  positive hemi-ortho-prism or orthodomal prism, or positive pinakoid of the second order, including the primary  $\{10\bar{1}\}$ . Each 2 faces.
- $\{0kl\}$  Right clino-prism or clino-dome, or right sphenoid of the first order, including the primary  $\{011\}$  ;  $\{0\bar{k}l\}$  left clino-prism or dome, or left sphenoid of the first order, including the primary  $\{0\bar{1}1\}$ . Each 2 faces.
- $\{hkl\}$  Right negative monoclinic sphenoid (of the fourth order), including the primary  $\{111\}$  ;  $\{h\bar{k}l\}$  left negative form, including the primary  $\{1\bar{1}1\}$  ;  $\{hkl\}$  right positive form, including the primary  $\{11\bar{1}\}$  ;  $\{h\bar{k}l\}$  left positive form, including the primary  $\{1\bar{1}\bar{1}\}$ . Each 2 faces.

The best example of this class of symmetry is afforded by tartaric

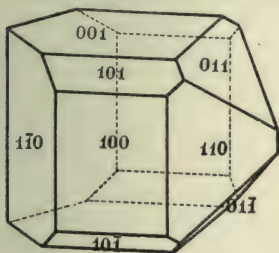


FIG. 211.—Dextro (Ordinary) Tartaric Acid.

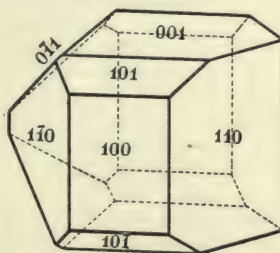


FIG. 212.—Lævo Tartaric Acid.

acid (Figs. 211 and 212),  $C_4H_6O_6$ , which exhibits combinations of  $\{100\}$ ,  $\{001\}$ ,  $\{101\}$ ,  $\{10\bar{1}\}$ ,  $\{110\}$ ,  $\{1\bar{1}0\}$ ,  $\{011\}$ , and  $\{0\bar{1}1\}$ . Two optically



active and enantiomorphous varieties are known, which were investigated by Pasteur in a research which attracted great attention at the time (see Chapter LV.), and will ever be of highly historic interest as being the pioneer of such researches, having for their object the separation and identification of the two enantiomorphous and oppositely optically active forms of the same chemical substance. The two modifications are shown in Figs. 211 and 212. The right-handed and dextro-rotatory variety, Fig. 211, is obviously the mirror-image of the left-handed or lævo-rotatory variety exhibited in Fig. 212, and the two are respectively distinguished by the presence of only one of the two clino-prisms, the dextro variety (Fig. 211) exhibiting the right form  $\{011\}$  and the lævo (Fig. 212) variety showing only the left form  $\{0\bar{1}1\}$ . The two ends of the symmetry axis also exhibit opposite pyro-electric properties, as is usual with hemimorphic crystals. The ratio of the axes, as determined by De la Provostaye, who reinvestigated the substance after Pasteur, is  $a : b : c = 1.2747 : 1 : 1.0266$ , and the axial angle  $\beta = 100^\circ 17'$ .

*Class 3.—Monoclinic Domal Class. Monoclinic-Hemihedral Class.*  
*Type, symmetrical about a Plane.*

Of the two elements of monoclinic symmetry the plane of symmetry is here alone operative, while the digonal axis is dormant. The symmetry conditions and the poles of one variety of the general form  $\{hkl\}$  are shown in Fig. 213.

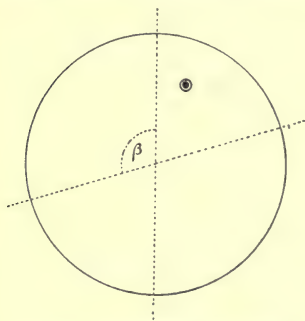


FIG. 213.—Symmetry Element and General Form of Class 3.

As in the last class, this form consists of only a pair of faces, which, however, are now symmetrical to the plane of symmetry, instead of being both on one side of the latter as in class 4. There will thus be four varieties of this general form, corresponding to the four angles made by the intersection of the axes  $a$  and  $c$ , a pair of faces with poles above and below each other in the same angle being comprised in each. The symbols will be the following:  $\{hkl\}$  the upper negative form, with poles in the upper obtuse axial angle, and consisting of the faces  $(hkl)$  and  $(h\bar{k}l)$ ;  $\{h\bar{k}l\}$  the lower positive form, with poles in the lower acute axial angle, consisting of  $(hkl)$

and  $(h\bar{k}l)$ ;  $\{\bar{h}kl\}$  the lower negative form, with poles in the lower obtuse angle, consisting of  $(\bar{h}kl)$  and  $(\bar{h}\bar{k}l)$ ; and  $\{\bar{h}\bar{k}l\}$  the upper positive variety, the one actually shown in Fig. 213, with poles in the upper acute axial angle, consisting of  $(\bar{h}kl)$  and  $(\bar{h}\bar{k}l)$ . These four forms are termed domes, and they are domes of the fourth order, according to the classification of von Groth and Fedorov. The domal edge always lies in the symmetry plane. The four primary domes are thus  $\{111\}$ ,  $\{1\bar{1}\bar{1}\}$ ,  $\{\bar{1}1\bar{1}\}$ , and  $\{\bar{1}\bar{1}1\}$ .

When the pole has migrated on to the sides  $(100) : (010)$  and  $(010) : (001)$  of the fundamental triangle, the hemihedral representative of the monoclinic prism or the clino-prism respectively produced will also consist of only two faces symmetrical to the plane of symmetry, instead of the holohedral four faces. In the case of the former we shall have two hemi-prisms or domes of the third order with the symbols  $\{hk0\}$  and  $\{\bar{h}k0\}$ , the first consisting of  $(hk0)$  and  $(h\bar{k}0)$ , and the second of  $(\bar{h}k0)$  and  $(hk0)$ . In the case of the latter we have two clino-domes, which are domes of the first order,

having the symbols  $\{0kl\}$  and  $\{0k\bar{l}\}$ ; the first will consist of  $(0kl)$  and  $(0\bar{k}l)$  and the second of  $(0k\bar{l})$  and  $(0kl)$ .

All forms with poles on the primitive circle will consist of one face only, as the digonal axis is absent. Hence we have two pedions together making up the holohedral basal pinakoid, ortho-pinakoid, and hemi-ortho-prism respectively. The clino-pinakoid, however, continues to be represented by both its faces, one above and one below the symmetry plane.

In résumé, we have consequently the following forms to distinguish in this class :

*List of Forms in Class 3.*

- $\{001\}$  Upper basal plane or pedion, or third positive pedion;  $\{00\bar{1}\}$  lower basal plane or pedion, or third negative pedion. Each 1 face.
- $\{100\}$  Front ortho-pedion, or first positive pedion;  $\{\bar{1}00\}$  back ortho-pedion, or first negative pedion. Each 1 face.
- $\{010\}$  Clino-pinakoid or second pinakoid. 2 faces.
- $\{hko\}$  Front hemi-prism, or dome of the third order, including the primary prism  $\{110\}$ ;  $\{h\bar{k}o\}$  back hemi-prism, or dome of the third order, including the primary  $\{\bar{1}10\}$ . Each 2 faces.
- $\{h0l\}$  Upper negative ortho-pedion, or pedion of the second order, including the primary  $\{101\}$ ;  $\{h0\bar{l}\}$  lower positive ortho- or second order pedion, including the primary  $\{\bar{1}0\bar{1}\}$ ;  $\{\bar{h}0\bar{l}\}$  lower negative ortho- or second order pedion, including the primary  $\{\bar{1}01\}$ ;  $\{\bar{h}0l\}$  upper positive ortho- or second order pedion, including the primary  $\{\bar{1}01\}$ . 1 face each.
- $\{0kl\}$  Upper clino-dome, or dome of the first order, including the primary  $\{011\}$ ;  $\{0k\bar{l}\}$  lower form of same, including the primary  $\{01\bar{1}\}$ . Each 2 faces.
- $\{hkl\}$  Upper negative dome, or dome of the fourth order, including the parametral primary dome  $\{111\}$ ;  $\{hk\bar{l}\}$  lower positive form, including the primary  $\{11\bar{1}\}$ ;  $\{\bar{h}k\bar{l}\}$  lower negative form, including the primary  $\{\bar{1}1\bar{1}\}$ ;  $\{\bar{h}kl\}$  upper positive form, including the primary  $\{\bar{1}11\}$ . Each 2 faces.

Potassium tetrathionate,  $K_2S_4O_6$ , is one of the few substances crystallising in this class of symmetry. Fig. 214 shows a crystal of this salt, on which are developed the forms  $\{100\}$ ,  $\{\bar{1}00\}$  (behind),  $\{110\}$ ,  $\{\bar{1}10\}$  (behind),  $\{001\}$ ,  $\{011\}$ ,  $\{11\bar{1}\}$ ,  $\{133\}$ , and  $\{\bar{1}11\}$  (behind). The indices attached to dotted lines in the figure refer to the back faces of the crystal. The ratio of the axes is  $a : b : c = 0.9302 : 1 : 1.2666$ , and the axial angle  $\beta = 104^\circ 16'$  according to the measurements of Fock.

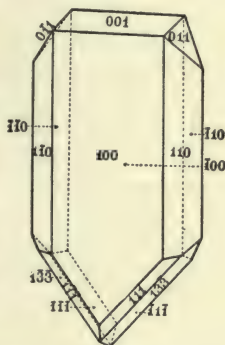


FIG. 214.—Crystal of Potassium Tetrathionate.

Generally it is only by the nature of the etched figures on the faces of the primary forms, particularly those of the primary prisms, that full evidence can be obtained that a monoclinic crystal belongs to this class, as it may happen that the complementary hemi-forms may both be developed, and the symmetry thus simulate that of the holohedral class 5.

## CHAPTER XVII

### PRACTICAL EXAMPLE OF A MONOCLINIC CRYSTAL

#### Ammonium Magnesium Sulphate, $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2, 6\text{H}_2\text{O}$ .

##### *Class 5, Monoclinic-Holohedral.*

THIS salt is chosen for the monoclinic example to be worked through in detail because it can so readily be obtained in excellent crystals, from a solution containing the molecularly equivalent weights of magnesium sulphate and ammonium sulphate, taking the precautions mentioned in

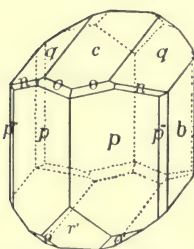


FIG. 215.—The measured Crystal of Ammonium Magnesium Sulphate.

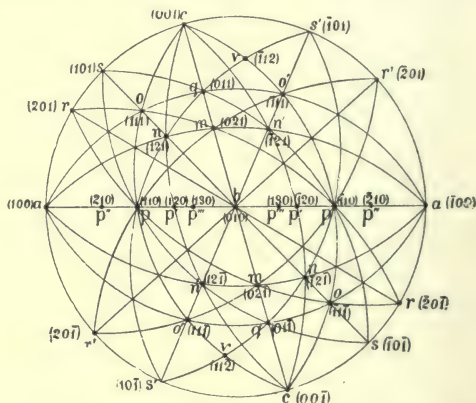


FIG. 216.—Stereographic Projection of Ammonium Magnesium Sulphate.

Chapter II. ; and also because the series of double salts, of which it forms one of the most convenient members for the purpose, exhibits very clearly typical holohedral monoclinic symmetry, and is one of the most important series of double salts known to us.

An illustration of the individual crystal chosen is given in Fig. 215, drawn to scale by the conventional parallel-perspective method to be fully explained, with constructional drawing, Fig. 356, in Chapter XXV., from a careful freehand drawing made at the time of the measurement of the crystal. Its stereographic projection is also given in Fig. 216,



and the mode of constructing it will be described as we proceed with the measurement of the various zones.

The crystal was a brilliant-faced perfectly transparent and colourless one, about three millimetres in length along the prism axis, and two millimetres thick.

The prism zone was obviously the one first inviting measurement. The crystal was set on the wax of the crystal-holder with the prism axis parallel to the goniometer axis, and with the broad plane  $b$  arranged parallel to one of the adjusting movements, and was then adjusted with the aid of the opposite screw, that of the other rectangularly arranged adjusting segment, so that the image of the signal-slit reflected from the plane  $b$  was symmetrical to the horizontal spider line of the eyepiece; then afterwards one of the adjacent prism faces was similarly adjusted with the aid of the other screw and movement, and a final touch given to the adjustment of  $b$  which had been thereby slightly disturbed. When this was achieved the whole of the faces of the prism zone were in adjustment, and gave the measurements detailed in the following table. The two  $p'''$  faces were only narrow strips, and one of them did not give trustworthy reflections, but the other gave quite good ones.

PRISM ZONE [ $bp$ ].

Circle Readings.		Angles.	
$b$	360° 0' A	$bp$	54° 40'
$p$	305 20	$pp$	70 35
$p$	234 45 A	$pb$	54 44 A
$b$	180 1 A	$bp$	54 46 A
$p$	125 15 A	$pp$	70 31 A
$p$	54 44 A	$pp'''$	29 26
$p'''$	25 18	$p'''b$	25 18
$b$	0 0 A		$pb$ 54° 44' A

An inspection of these angular values undoubtedly indicates that the same angle of fifty-four degrees and about forty minutes occurs symmetrically repeated four times in the circle, once in each quadrant. We shall see this very clearly if we plot out the values along a primitive circle, as usual for a prism zone in the first instance, whether it is permanently to form the primitive-circle-zone or not. That the four values of  $bp$  are really intended to be identical is clear from the closeness of the three "A" values, which only differ by 2'. It was on account of this symmetry that the four  $p$ -faces were all marked with the same letter  $p$ ; and the two  $b$ -faces were obviously parallel and hence were both distinguished by the same letter.

We can, therefore, legitimately take the mean of these three values of  $bp$ , and even include the fourth value as it is also so close, and the value was all but an "A" value. The resulting mean value of  $bp$  is 54° 44'. The mean of the two values of  $pp$  is similarly 70° 33'. The face of the other prismatic form is labelled  $p'''$  rather than  $p'$  because in the cases of other salts of the same isomorphous series  $p'$  and  $p''$  are both appropriated to denote other forms developed in the prism zone. Such a crystal exhibiting  $p'$  and  $p''$  is that of potassium nickel sulphate shown in Fig. 216a.



themselves, and also with respect to the intersections of this third zone plane with the other two. We should next, therefore, measure the zone in question, which is the one containing the  $c$  and  $r'$  faces. We cannot construct the stereographic projection until we have done so; all that we can at present do is to draw a circle, quite independent of that already drawn to represent the prism zone, and arrange the poles  $b$ ,  $q$ , and  $c$  symmetrically along it. But the relationship of this zone circle to the prism zone we do not yet know. In the zone in question the only faces developed on the crystal were those marked  $c$  and  $r'$  in Fig. 215.

The crystal was now reset on the wax, on a  $b$ -face, which is perpendicular to the zone of faces in question, and with a  $c$ -face parallel to one of the movements. After adjustment of both  $c$  and  $r'$  faces, and centring as usual, the following measurements were obtained:

 MEASUREMENTS FOR THE ZONE  $[cr']$ .

Circle Readings.	Angles.
$\left\{ \begin{array}{l} c \ 360^\circ \ 0'A \\ r' \ 244 \ 27 \end{array} \right.$	$\left\{ \begin{array}{l} cr' \ 115^\circ \ 33' \\ r'c \ 64 \ 27 \end{array} \right.$
$\left\{ \begin{array}{l} c \ 180 \ 0 \ A \\ r' \ 64 \ 25 \ A \end{array} \right.$	$\left\{ \begin{array}{l} cr' \ 115 \ 35 \ A \\ r'c \ 64 \ 25 \ A \end{array} \right.$

It was fairly obvious from a mere inspection of the crystal, that the angle  $cr'$  of  $115^\circ \ 34'$  (the mean of the two values) is not bisected by the pole, that of a possible face, at the intersection of the zone  $[bp]$  with the zone  $[cr']$ . The possible face in question is actually developed on many of the salts of this isomorphous series, particularly on potassium magnesium sulphate, on the crystals of which it is often quite prominent, as shown in Fig. 217, which is taken from the author's first memoir<sup>1</sup> on the subject of these salts. It is also shown less prominently on the crystal of potassium nickel sulphate illustrated in Fig. 216a.

It is marked with the letter  $a$ , both in these illustrations of the potassium magnesium and potassium nickel salts and in the stereographic projection common to the whole series given in Fig. 216. When the crystal now under consideration was set up with the prism axis, and therefore with the faces  $b$  and  $p$ , vertical, it was clear that the faces  $c$  and  $r'$  were not inclined equally to the vertical, the inclination of  $c$  being markedly greater (nearer to  $90^\circ$ ) than that of  $r'$ . If the face  $a$  had been present on the crystal of ammonium magnesium sulphate before us, we could at once have verified this fact and determined the actual inclinations. It would appear certain, however, that only centro-

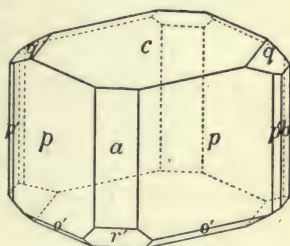


FIG. 217.—Crystal of Potassium Magnesium Sulphate.

<sup>1</sup> Journ. Chem. Soc. Trans., 1893, 63, 345.



symmetry, causing the presence of pairs of parallel faces, is present in the  $cr'$  zone just measured, and we can, therefore, at any rate preliminarily, assume that the crystal is not orthorhombic, but monoclinic, the symmetry plane being that already found, namely, parallel to the  $b$ -faces, and which is the zone-plane of, and therefore perpendicular to, the zone  $cr'$ .

As in the stereographic projection of monoclinic crystals we take the symmetry plane for the plane of projection, we can at once draw in the real primitive circle, on which the poles  $c$  and  $r'$  are to appear. The two zones  $[bp]$  and  $[bqc]$  previously measured will appear in the projection as diameters, intersecting at the centre, which will be the pole of the face  $b$ . The prism zone  $[bp]$  is to be the horizontal diameter, for its faces and edges are parallel to the axis which we take for the vertical one. We can, therefore, at once place on it the poles  $p$  and  $p''$ , finding them by the method already several times explained, of marking off the angles on the primitive circle, and joining the points thus marked off to the pole of the zone, which is the opposite extremity of the diameter (in this case only constructional and afterwards erased) at right angles to the zonal diameter on which we are finding the poles. The extremities of this  $bp$ -zonal diameter, where it meets the primitive circle, would be the poles of the  $a$ -faces if they were developed.

In order to find the position of the other measured zone  $[bqc]$ , on which we as yet only know the position of the pole  $b$  at the centre, we require to know the position of the extremity-poles  $c$ , at the intersection of the zone with the primitive circle. The angle  $ac$  would at once fix it, but the  $a$ -faces being absent we cannot measure the angle directly, and our knowledge of the angle  $cr'$ , in the third zone measured, does not help us, because  $c$  and  $r'$  may still be anywhere, separated at this angle, on the primitive circle. We know, however, that the two  $p$ -faces shown on the projection are accompanied by two others symmetrical to the plane of projection, and therefore situated immediately underneath them and represented by the same dot in each case, or by a ring round each dot. If, therefore, we draw a circular arc to pass through the three points  $c$  (assuming for the moment an approximate position for  $c$ ),  $p$ , and the parallel  $c$ , the arc will really represent two zones, passing through the dot-pole  $p$  and the ring-pole  $p$  respectively, and intersecting at each of the two  $c$ -poles. Now if our supposition be correct that the plane of projection is really a plane of symmetry perpendicular to the zone  $cr'$ , the two shorter arcs  $cp$ , as well as of course the two longer supplementary arcs  $cp$ , will be equal; translated into actual facts on the crystal this means that the angle between the face of basal-pinakoidal character  $c$  and the prism face on its right front, and the similar angle between the same  $c$ -face and the prism face on its left front, will be equal. This we can at once test by measurement, and when we have determined the actual magnitude of the angle we can use it in conjunction with our knowledge of the angle  $ap$ , for this is the complement of the actually measured  $bp$ , to calculate the required angle  $ac$ . Our next task, therefore, is to measure the two zones  $[cp]$ .

The same setting of the crystal on the wax as for the zone  $cr'$  can be retained, and first one and then the other zone may be adjusted and measured, by use chiefly of one

only of the adjusting movements, the other being only required to perfect the adjustment of the *c*-face, which had been set approximately perpendicularly to it. When this had been actually done for the crystal under investigation, and the *c* and *p* faces were in precise adjustment parallel to the goniometer axis, it was found that besides the two pairs of parallel *c* and *p* faces there were also in automatic adjustment, as belonging to the same zone, several faces of the forms *o* and *o'*. The actual measurements were as follows :—

Readings.	Angles.	Readings.	Angles.
$\left\{ \begin{array}{l} p \ 360^\circ \ 0'A \\ o' \ 300 \ 44 \ A \\ c \ 256 \ 10 \ A \\ p \ 180 \ 0 \ A \\ o' \ 120 \ 38 \ A \\ c \ 76 \ 8 \ A \\ o \ 42 \ 35 \\ p \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} po' \ 59^\circ \ 16'A \\ o'c \ 44 \ 34 \ A \\ cp \ 76 \ 10 \ A \\ po' \ 59 \ 22 \ A \\ o'c \ 44 \ 30 \ A \\ co \ 33 \ 33 \\ op \ 42 \ 35 \end{array} \right.$	$\left\{ \begin{array}{l} p \ 360^\circ \ 0'A \\ o \ 317 \ 26 \\ c \ 283 \ 55 \ A \\ o' \ 239 \ 24 \ A \\ p \ 180 \ 1 \ A \\ c \ 103 \ 55 \ A \\ o' \ 59 \ 21 \ A \\ p \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} po \ 42^\circ \ 34' \\ oc \ 33 \ 31 \\ co' \ 44 \ 31 \ A \\ o'p \ 59 \ 23 \ A \\ pc \ 76 \ 6 \ A \\ co' \ 44 \ 34 \ A \\ o'p \ 59 \ 21 \ A \end{array} \right.$

Collecting together the values of similar angles afforded by the parallel faces of the same zone, together with the pairs of analogous angles yielded by the other zone, it will be at once clear that the angle *cp* on the right zone is intended to be identical with the angle *cp* on the left zone. For the two angles in question are those formed by the *c* and *p* faces shown in our drawing of the crystal, Fig. 215, and the edges *cp* of which are modified by the little *o*-faces, and their values, as shown in the table of measurements, are respectively  $76^\circ 8'$  and  $76^\circ 5'$ , obviously too near together to be intended to be different. Hence, to get the real value of the angle we may now, having decided on their symmetry with respect to the symmetry plane, with propriety take the mean of all the four values of *cp* yielded by the two zones, and consequently also take the mean of all the other similar angles, afforded by parallel faces of the same zone or corresponding faces of the two zones. These mean values are :  $cp = 76^\circ 7'$ ,  $co = 33^\circ 32'$ ,  $op = 42^\circ 35'$ ,  $po' = 59^\circ 21'$ ,  $o'c = 44^\circ 32'$ .

It will be convenient to state here that the crystal under measurement was one of eleven exceptionally perfect ones employed on the detailed investigation<sup>1</sup> of the crystallography of this salt. The work on the other ten crystals fully confirmed the conclusion as to the symmetry, in confirmation of older work on the salt, and in many cases the two *cp* values for the two sides of the symmetry plane were within not only  $3'$  but  $1'$ .

We are now in a position to find by calculation the value of the angle *ac* in the primitive circle zone, and so to fix the position of the poles *c*, which at present we only know approximately.

If we draw a rough stereographic projection in freehand, similar to Fig. 216, assuming the latter not yet to have been drawn accurately owing to lack of knowledge of the angle we are about to calculate, we can use the spherical triangle *acp* for the purpose of the calculation in question. For in this triangle the angle at *a* is a right angle, and we know the sides *ap* and *cp* to be respectively  $90^\circ - bp = 35^\circ 16'$  and  $76^\circ 7'$ .

<sup>1</sup> Journ. Chem. Soc., 1905, 87, 1132.

Constructing a Napierian diagram, as in Fig. 53 (page 107), we at once deduce therefrom by Napier's rules :

$$\begin{aligned}\cos 76^\circ 7' &= \cos ac \cos 35^\circ 16', \\ \text{or } \cos ac &= \frac{\cos 76^\circ 7'}{\cos 35^\circ 16'} \quad ac = 72^\circ 54' .\end{aligned}$$

We can now continue the accurate construction of the stereographic projection already commenced, by inserting the *c*-poles on the primitive circle at  $72^\circ 54'$  from the *a*-poles, and joining them by the diameter *cbc*. On this diameter, which will form the projection of the zone [*cqb*], the positions of the *q*-poles should be found, similarly to the *p*-poles on the zone [*bp*], by the usual process already alluded to. We can then construct accurately the two arc-zones [*cpc*], one on each side of the diameter. We have next to find the positions on these arc-zones of the poles *o* and *o'*. This we are enabled to do very easily, for if we adjust on the goniometer, parallel to one of the movements, the face *r'* instead of the *c*-face, and again the same *p*-face parallel to the other movement, we find that in the complete arc-zone [*r'p*] there are also automatically adjusted two *o'* faces. In other words, the poles of the *o'* faces are at the intersections of the arc-zones [*cpc*] and [*r'pr'*]. If we now construct a further pair of arc-zones on each side of the horizontal diameter, to pass through the three points *a*, *q*, and *a*, we shall find that they also pass through the *o'*-poles, and where the arcs intersect the shorter *cp* arcs (the arcs  $76^\circ 7'$ ) will be the positions of the *o*-poles, if they are, as seems likely from the appearance of the crystal and as will shortly be proved to be the fact, those of the hemi-pyramid faces complementary to the *o'*-faces.

Having thus fixed the position of all the principal facial poles, leaving in fact only the faces *n* still to be located, we may now decide on what further zones require measurement. We should draw diameters through the *b* and *o* poles, and through the *b* and *o'* poles, and then measure first those two further diametral zones. On measuring the former, we shall discover the *n* poles in the zone, and can mark off their positions by the usual process already referred to. Then we ought certainly to measure the important pair of zones [*r'o'pr'*], which have enabled us to locate so many poles. And finally, there are two pairs of zones between the well-developed *p* and *q* faces, and one pair of these, having the shorter *pq* arc, will be found to contain also the *n*-faces, as will be obvious from the fact that these narrow *n*-faces modify the edges *qp* in the drawing, Fig. 215. The intersection of this pair of zones with the [*bno*] zone thus finally confirms the position of the *n*-poles, and completes the stereographic projection.

The actual circle readings and angular values obtained for one of each of these five pairs of zones will now be given. Similar angles were afforded by the complementary five zones, the details of which it is unnecessary to quote.

In the case of the first zone [*bno*] only one value, that of the angle *bo*, was sufficiently trustworthy to record, the angles *bn* and *no* being only determinable approximately, owing to the poor quality of the reflection from the *n*-faces; the images were sufficiently clearly visible, however, to render it certain that the *n*-faces belonged to the zone. In the zone [*pnq*] the images afforded by the *n*-faces were much sharper, and consequently trustworthy.



Zone [bno].		Zone [bo'].	
Readings.	Angle.	Readings.	Angles.
$\left\{ \begin{array}{l} b \ 360^{\circ} \ 0'A \\ o \ 289 \ 9 \end{array} \right.$	$bo \ 70^{\circ} \ 51'$	$\left\{ \begin{array}{l} b \ 360^{\circ} \ 0'A \\ o' \ 294 \ 36 \ A \\ o' \ 245 \ 19 \ A \\ b \ 180 \ 0 \ A \\ o' \ 114 \ 40 \ A \\ o' \ 65 \ 24 \ A \\ b \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} bo' \ 65^{\circ} \ 24'A \\ o'o' \ 49 \ 17 \ A \\ o'b \ 65 \ 19 \ A \\ bo' \ 65 \ 20 \ A \\ o'o' \ 49 \ 16 \ A \\ o'b \ 65 \ 24 \ A \end{array} \right.$

Zone [r'o'p].		Zone [pq].		Zone [pnq].	
Readings.	Angles.	Readings.	Angles.	Readings.	Angles.
$\left\{ \begin{array}{l} p \ 360^{\circ} \ 0'A \\ o' \ 268 \ 26 \ A \\ r' \ 233 \ 10 \ A \\ p \ 180 \ 3 \ A \\ o' \ 88 \ 29 \\ r' \ 53 \ 9 \\ p \ 0 \ 1 \ A \end{array} \right.$	$\left\{ \begin{array}{l} po' \ 91^{\circ} \ 34'A \\ o'r' \ 35 \ 16 \ A \\ r'p \ 53 \ 7 \ A \\ po' \ 91 \ 34 \\ o'r' \ 35 \ 20 \\ r'p \ 53 \ 8 \end{array} \right.$	$\left\{ \begin{array}{l} p \ 360^{\circ} \ 0'A \\ q \ 271 \ 39 \ A \\ p \ 180 \ 0 \ A \\ q \ 91 \ 38 \ A \\ p \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} pq \ 88^{\circ} \ 21'A \\ qp \ 91 \ 39 \ A \\ pq \ 88 \ 22 \ A \\ qp \ 91 \ 38 \ A \end{array} \right.$	$\left\{ \begin{array}{l} q \ 360^{\circ} \ 0'A \\ n \ 234 \ 2 \\ p \ 297 \ 34 \ A \\ q \ 180 \ 2 \ A \\ p \ 117 \ 35 \ A \\ q \ 0 \ 0 \ A \end{array} \right.$	$\left\{ \begin{array}{l} qn \ 25^{\circ} \ 58' \\ np \ 36 \ 28 \\ qp \ 62 \ 26 \ A \\ pq \ 117 \ 32 \ A \\ qp \ 62 \ 27 \ A \\ pq \ 117 \ 35 \ A \end{array} \right.$

The mean values derived from the five pairs of zones were :  $bo=70^{\circ} \ 51'$  ;  $bo'=65^{\circ} \ 22'$  ,  $o'o'=49^{\circ} \ 16'$  ;  $po'=91^{\circ} \ 36'$  ,  $o'r'=35^{\circ} \ 18'$  ,  $r'p=53^{\circ} \ 6'$  ;  $pq=88^{\circ} \ 21'$  ,  $qp=91^{\circ} \ 39'$  ;  $qp=62^{\circ} \ 25'$  ,  $qn=25^{\circ} \ 58'$  ,  $np=36^{\circ} \ 28'$  ,  $pq=117^{\circ} \ 35'$  .

This completes the measurements. A final list of the mean measured angles, in their proper order in the various zones, will be found at the end of the chapter, alongside the values calculated from the three most reliably measured basal angles, three being required for the calculation of monoclinic crystals, as stated in Chapter VII.

Before passing to the calculations, a word or two must be said about the symmetry, and the indices of the faces. It has been fully proved that the plane parallel to the *b*-faces is a symmetry plane, and no other symmetry plane has been discovered with respect to the crystal. Hence, presumably, the symmetry is monoclinic. The disposition of angles in the zone of the primitive circle confirms this view, for it is not similar to the zones [*apb*] and [*bqc*] in exhibiting angles symmetrical about *a* and about *c*, each face being only accompanied by its parallel companion and not by a fellow symmetrically arranged with respect to either of the primary faces just mentioned. The symmetry exhibited in the zones [*apb*] and [*bqc*] is demanded if *b* be really a symmetry plane, for if any *p* or *q* face in the top hemisphere be considered, for instance, a second face is required, immediately underneath it, in the lower hemisphere of the projection, and might be indicated by a ring round the dot representing *p* or *q* in the upper hemisphere. Similarly, any pole whatsoever on the projection, other than one on the primitive circle, must be accompanied by a symmetrical fellow in the lower hemisphere, so that if

the lower hemisphere poles were actually drawn in they would all appear as rings round the dots representing in the usual manner the poles on the upper hemisphere. Our measurements have fully confirmed this, every are on the upper hemisphere having its equal companion on the lower. The great advantage will now also be apparent of choosing the plane of symmetry for the plane of projection.

It will be shown later in Chapters XLV., XLVI., and XLVIII. that the conclusion as to the monoclinic nature of the symmetry is fully borne out by the optical properties of the crystal.

As regards the facial indices. The  $b$ -faces parallel to the plane of symmetry are chosen as, and are in fact obviously, those of the clinopinakoid  $\{010\}$ , the indices of the upper face in the projection, the right face in Fig. 215, being  $(010)$ , and those of the lower  $(\bar{0}10)$ . As is customary in drawing the projection of monoclinic crystals, the possible front face of the orthopinakoid  $a = \{100\}$  is placed at the left end of the horizontal diameter in the projection. The position of this possible face will be rendered clear by the illustration of the crystal of potassium magnesium sulphate given in Fig. 217, which shows the face  $(100)$  well developed in the foreground on the front of the crystal; it is also shown on the crystal of potassium nickel sulphate represented in Fig. 216*a*. The parallel orthopinakoid face at the back of the crystal, the pole of which is placed at the right end of the horizontal diameter in the projection, is  $(\bar{1}00)$ . The edges of intersection of  $a$  and  $b$  faces, or of  $b$  and  $p$  faces, all of which edges are parallel to each other, are parallel to the vertical axis  $c$  of the crystal, indeed these edges are chosen as the direction of the vertical axis. The faces  $c$ , situated as we have seen at  $72^\circ 54'$  from the  $a$ -faces, are chosen as those of the basal pinakoid  $\{001\}$ , the upper one being  $(001)$  and the lower parallel one  $(00\bar{1})$ , and their edges of intersection with the  $b$ -faces, or with the  $q$ -faces (all these edges being mutually parallel), mark the direction of the inclined crystallographic axis  $a$ . The symmetry (digonal) axis is the normal to the clinopinakoid  $b = \{010\}$  and is the crystallographic axis  $b$ , indicated by the central dot of the projection which also marks the pole of  $b = (010)$ .

The most prominent faces of prismatic character,  $p$  and  $q$ , are taken respectively as those of the primary monoclinic prism  $\{110\}$  and the primary clino-prism  $\{011\}$ . Now it has been shown that the shorter zonal arcs  $cp$  and  $aq$  intersect at the poles of the  $o$ -faces, and therefore the latter are those of the parametral form  $\{111\}$ , the negative monoclinic hemipyramid. If any doubt arise, or the fact be not sufficiently obvious, it can immediately be proved by cross-multiplication of the symbols of the two zones, as under :

$$\begin{array}{rcl}
 001001 & & 100100 \\
 \times \times \times & = & \bar{1}10 \\
 110110 & & 011011 \\
 & & \bar{1}10\bar{1}10 \\
 & \times \times \times & = 111. \\
 & 0\bar{1}10\bar{1}1 &
 \end{array}$$

Similarly, the longer arcs  $cp$  and  $aq$  intersect at the  $o'$  poles, and these are consequently those of the faces of the form  $\{11\bar{1}\}$ , the positive monoclinic hemi-pyramid. The indices of the forms  $r'$ ,  $p'''$ , and  $n$  will be determined during the course of the calculations. It may be preliminarily stated that they will be shown to be those of the positive hemi-ortho-prism or pinakoid of the second order  $\{201\}$ , the monoclinic prism of the third order  $\{130\}$ , and the negative monoclinic hemi-pyramid  $\{121\}$ .

Having now fully indicated the nature of the symmetry and the disposition and character of the faces present on the crystal, as well as having completely constructed the stereographic projection, we are in a position to proceed at once to the calculations of angles and elements.

### Calculation of Angles and Elements.

$$\begin{aligned}\text{Basal angles : } bp &= (010) : (110) = 54^\circ 44', \\ cp &= (001) : (110) = 76^\circ 7', \\ bq &= (010) : (011) = 64^\circ 49' .\end{aligned}$$

These three were chosen as basal angles because of their being most trustworthy, as furnished by uniformly excellent faces, and as being the most frequently measured of all the principal angles, not only on the individual crystal taken as our example, but on all the eleven crystals employed during the exhaustive investigation of this salt which has been referred to, and of which our example was one of the most perfect. The mean values of 39 and 32 measurements respectively of  $bp$  and  $cp$  are identical with the mean values furnished by our example. The mean value of 40 measurements of  $bq$  is  $1'$  larger than was afforded by our example, which was  $64^\circ 48'$ .

From the values of  $bp$  and  $bq$  we can at once find the values of  $ap = (100) : (110)$  and  $cq = (001) : (011)$  by difference from  $90^\circ$ ,  $ap$  being  $35^\circ 16'$  and  $cq$  being  $25^\circ 11'$ . The former was unmeasurable on account of the absence of any  $a$ -faces, but the angle  $pp = (110) : (1\bar{1}0)$ , its double, was measured 19 times, and its mean value found to be  $70^\circ 34'$ . The mean of the two values yielded by our example has been shown to be  $70^\circ 33'$ . The half of these is  $35^\circ 17'$ , which corresponds to  $ap$ . The mean of the four values of  $cq$  yielded by our crystal was  $25^\circ 12'$ , and of 40 values derived from the whole eleven crystals  $25^\circ 11'$ .

The Axial Angle  $\beta = ac = (100) : (001)$  has already been calculated, for the purpose of drawing the projection, from the mean values of the angles  $bp$  and  $cp$  derived from the measurements of the crystal before us, and as these values are identical with the above given basal angular values, the result, namely  $ac = 72^\circ 54'$ , stands valid for the final value of  $ac$ . This is the acute angle between the vertical and inclined axes, and the obtuse angle usually quoted as the axial angle, being the angle in the upper right front octant, is obviously its supplement,  $107^\circ 6'$ .

The Axial Ratios.—We can find the axial ratios at once very conveniently by the general method given on page 111 in Chapter VII. In connection with Fig. 54 there given, which shows the general arrangement of the primary triangle formed by the poles of  $a = (100)$ ,  $b = (010)$ , and



$c=(001)$ , and the parametral triangles lying within it formed by arcs from the corners to the poles of  $(110)$ ,  $(011)$ , and  $(101)$ , and intersecting at the pole of  $(111)$ , it was shown that :

$$\frac{a}{b} = \frac{\sin \theta}{\sin \phi}, \quad \frac{c}{b} = \frac{\sin \psi}{\sin \chi}.$$

The general conditions thus defined for triclinic crystals in Fig. 54, and these values thence derived for the ratios  $a/b$  and  $c/b$ , when applied to the case of the monoclinic crystal before us simplify considerably. The primary triangle  $a=(100):b=(010):c=(001)$  is equally well given by the stereographic projection, and that part of the latter comprising this triangle and the parametral triangles contained within it are separately given for the sake of clearness in Fig. 218, and the

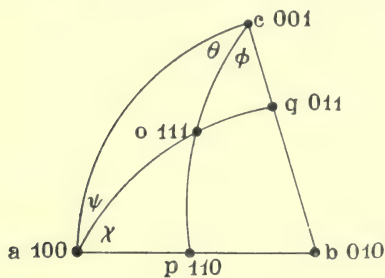


FIG. 218.

same Greek letters for the various angles are inserted as in Fig. 54. The angles  $\theta$  and  $\phi$  together make up  $90^\circ$ , and so also do  $\chi$  and  $\psi$ , so that the values for the said ratios simplify as under :

$$\frac{a}{b} = \frac{\sin \theta}{\sin \phi} = \frac{\sin \theta}{\cos \theta} = \tan \theta;$$

$$\frac{c}{b} = \frac{\sin \psi}{\sin \chi} = \frac{\sin \psi}{\cos \psi} = \tan \psi.$$

Now  $\theta$  is the angle at  $c$  in the triangle  $acp$ , which has a right angle at  $a$ , and in which we know the sides  $ac=72^\circ 54'$ ,  $cp=76^\circ 7'$ , and  $ap=35^\circ 16'$ .

Drawing the Napierian diagram as in Fig. 53, we deduce by the rules that :

$$\cos c = \cot 76^\circ 7' \tan 72^\circ 54'. \quad c = 36^\circ 30' = \theta.$$

$$\frac{a}{b} = \tan 36^\circ 30' = 0.7400.$$

Similarly, the angle  $\psi$  is the angle at  $a$  in the triangle  $acq$ , which has a right angle at  $c$ , and in which we know the sides  $ac=72^\circ 54'$  and  $cq=25^\circ 11'$ . We can at once find its value, as in the case of  $\theta$ , by constructing a diagram and applying Napier's rules, as follows :

$$\cot a = \sin 72^\circ 54' \cot 25^\circ 11'. \quad a = 26^\circ 11\frac{1}{2}' = \psi.$$

$$\frac{c}{b} = \tan 26^\circ 11\frac{1}{2}' = 0.4918.$$

Hence :

$$a : b : c = 0.7400 : 1 : 0.4918.$$

**Calculation of Angles** (Stereographic projection, Fig. 216).—We can begin most conveniently by finding  $aq=(100):(011)$ , for this angle can be calculated from the triangle just considered, from the Napierian diagram for which we derive :

$$\cos aq = \cos 25^\circ 11' \cos 72^\circ 54'. \quad aq = 74^\circ 34'.$$

This angle was not measured, as no  $a$ -faces were developed.

**To find  $pq=(110):(011)$ .** This angle can next be found from the triangle  $bqp=(010):(011):(110)$ . This triangle is not right-angled, but we cannot expect to find right-angled triangles so plentiful in monoclinic crystals as we did in the case of rhombic crystals. We must employ, therefore, the formulæ of (b) on page 109 of Chapter VII. In the triangle in question we know that the angle at  $b$  is equal to  $ac=72^\circ 54'$ , and we also know the sides including this angle, namely,  $bp=54^\circ 44'$  and  $bq=64^\circ 49'$ . Applying the formulæ we have :

$$\begin{aligned}\tan \theta &= \tan bp \cos ac, & \cos pq &= \frac{\cos bp \cos (bq - \theta)}{\cos \theta} \\ \tan \theta &= \tan 54^\circ 44' \cos 72^\circ 54'. & \cos pq &= \frac{\cos 54^\circ 44' \cos (64^\circ 49' - \theta)}{\cos \theta} \\ \theta &= 22^\circ 34'. & pq &= 62^\circ 26' .\end{aligned}$$

The mean measured value of  $pq$  was  $62^\circ 25'$ , as derived from the crystal now under consideration, and  $62^\circ 26'$  for all eleven crystals.

To find  $po' = (110) : (11\bar{1})$  and  $ao' = (100) : (11\bar{1})$ .

We can calculate these two angles simultaneously by the formulæ at (c) on the same page of Chapter VII. just quoted, for finding the two sides when the two angles and the included side are known. In the triangle  $a = (100) : p = (110) : o' = (11\bar{1})$  we know the side  $ap = 35^\circ 16'$ , and the angle at  $a$  is the complement of the angle at  $a$  in the triangle  $acq$ , which has already been calculated for the purpose of finding the ratio of the axes and found to be  $26^\circ 11\frac{1}{2}'$ , so that the angle at  $a$  now required is  $63^\circ 48\frac{1}{2}'$ . The angle at  $p$  also required is the supplement of the angle denoted by that letter in the triangle  $acp$ , the same triangle as was employed for the calculation of the arc  $ac$  on page 263. Proceeding first to calculate this angle at  $p$  by Napier's rules we have :

$$\begin{aligned}\cos p &= \tan 35^\circ 16' \cot 76^\circ 7' \\ p &= 79^\circ 56'. \text{ Supplement} = 100^\circ 4' .\end{aligned}$$

Our conditions are now all fulfilled for the employment of formulæ (c), for we know the two angles  $a = 63^\circ 48\frac{1}{2}'$  and  $p = 100^\circ 4'$  and the side included by them  $ap = 35^\circ 16'$ , in the triangle under consideration  $apo'$ . Denoting the larger angle at  $p$  by the letter A of the formulæ, and the angle at  $a$  by B, we have :

$$\begin{aligned}A + B &= 100^\circ 4' + 63^\circ 48\frac{1}{2}' = 163^\circ 52\frac{1}{2}', \text{ and } \frac{1}{2}(A + B) = 81^\circ 56', \\ A - B &= 100^\circ 4' - 63^\circ 48\frac{1}{2}' = 36^\circ 15\frac{1}{2}', \text{ and } \frac{1}{2}(A - B) = 18^\circ 8' .\end{aligned}$$

Inserting these values in the formulæ we get :

$$\begin{aligned}\tan \frac{1}{2}(ao' + po') &= \frac{\cos 18^\circ 8'}{\cos 81^\circ 56'} \tan \frac{1}{2}(35^\circ 16') \\ \tan \frac{1}{2}(ao' - po') &= \frac{\sin 18^\circ 8'}{\sin 81^\circ 56'} \tan 17^\circ 38'\end{aligned}$$

$$\begin{aligned}\frac{1}{2}(ao' + po') &= 65^\circ 5'; & \frac{1}{2}(ao' - po') &= 5^\circ 42\frac{1}{2}'. \\ ao' + po' &= 130^\circ 10', & 2ao' &= 141^\circ 35', 2po' = 118^\circ 45' \text{ (by addition and subtraction),} \\ ao' - po' &= 11^\circ 25', & ao' &= 70^\circ 48', po' = 59^\circ 22' .\end{aligned}$$

The mean measured value of  $po'$  derived from the crystal under consideration was  $59^\circ 21'$ , and from all eleven crystals  $59^\circ 19'$ .

Two further angles at once follow from our knowledge of  $ao'$  and  $po'$ , namely,

$$\begin{aligned}o'q &= (11\bar{1}) : (01\bar{1}) = 180^\circ - (aq + ao') = 180^\circ - (74^\circ 34' + 70^\circ 48') = 34^\circ 38'. \\ o'c &= (11\bar{1}) : (00\bar{1}) = 180^\circ - (cp + po') = 180^\circ - (76^\circ 7' + 59^\circ 22') = 44^\circ 31' .\end{aligned}$$

The mean measured value of the latter angle on the crystal which forms our example was  $44^\circ 32'$ , and for the whole eleven crystals  $44^\circ 34'$ .

To find  $bo' = (010) : (11\bar{1})$  and  $o'o' = (11\bar{1}) : (11\bar{1})$ .

This we can do from the right-angled triangle  $abo' = (100) : (010) : (11\bar{1})$ , the side  $ab$  being the right angle, the angle at  $a$  having been shown to be  $63^\circ 48\frac{1}{2}'$ , and the side  $ao'$  having just been found to be  $70^\circ 48'$ . Constructing the Napierian diagram we deduce :

$$\begin{aligned}\cos bo' &= \sin 70^\circ 48' \cos 63^\circ 48\frac{1}{2}'. & bo' &= 65^\circ 22'. \\ o'o' &= 2(90^\circ - 65^\circ 22') = 49^\circ 16' .\end{aligned}$$

These values are identical with the mean of the measured values of  $bo'$  and  $o'o'$  respectively.

While dealing with this triangle, it will be convenient to calculate the angle at  $b$ , for it is the angle on the primitive circle between  $a = (100)$  and the possible face  $(10\bar{1})$ ,

the pole of which is situated on that circle at the end of the diameter  $bo'$ , and which has been found developed on several of the salts of the series, the form having been allotted the letter  $s'$ .

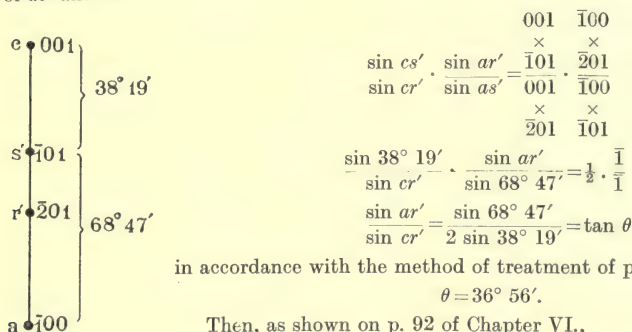
$$\sin b = \tan 63^\circ 48\frac{1}{2}' \cot 65^\circ 22'. \quad b = as' = 68^\circ 47'.$$

From this it follows that :

$$cs' = 180^\circ - (ac + as') = 180^\circ - (72^\circ 54' + 68^\circ 47') = 38^\circ 19'.$$

**To find  $cr' = (001) : (\bar{2}01)$  and  $ar' = (100) : (20\bar{1})$ .**

For this calculation we can conveniently employ the anharmonic ratio of the four poles in the zone  $c = (001)$ ,  $s' = (\bar{1}01)$ ,  $r' = (\bar{2}01)$ ,  $a = (\bar{1}00)$ . A preliminary use of the ratio, employing the measured value of  $cr'$  and the value of the total angle  $ac$ , the supplement of the already calculated angle  $ac$ , indicated that the indices of the form  $r'$  were  $\{\bar{2}01\}$ , and we now proceed to calculate the angles  $cr'$  and  $ar'$ , assuming these indices for  $r'$ . The conditions are shown in Fig. 219, for we have just found the values of  $as'$  and  $cs'$ .



in accordance with the method of treatment of p. 91, Chapter VI.  
 $\theta = 36^\circ 56'.$

Then, as shown on p. 92 of Chapter VI.,

$$\begin{aligned} \tan \frac{1}{2}(cr' - ar') &= \tan \frac{1}{2}(cr' + ar') \cdot \tan (45^\circ - \theta) \\ &= \tan \frac{1}{2}(107^\circ 6') \cdot \tan 8^\circ 4' \\ &= \tan 53^\circ 33' \tan 8^\circ 4' \end{aligned}$$

$$\frac{1}{2}(cr' - ar') = 10^\circ 52'.$$

We already know :  
 and we now find :

$$\begin{aligned} cr' + ar' &= 107^\circ 6', \\ cr' - ar' &= 21^\circ 44'. \end{aligned}$$

By adding :  $2cr' = 128^\circ 50'$ , and therefore  $cr' = 64^\circ 25'$ ;  
 and by subtracting :  $2ar' = 85^\circ 22'$ , and thus  $ar' = 42^\circ 41'$ .

The former of these two angles was measured, and the mean of the two values yielded by the excellent crystal which forms our example was  $64^\circ 26'$ , the two independent values being  $64^\circ 27'$  and  $64^\circ 25'$ . For the whole eleven crystals the mean was  $64^\circ 29'$ . This satisfactory agreement of the calculated and measured angle  $cr'$  finally confirms the indices  $\{\bar{2}01\}$  for the form  $r'$ .

**To find  $pr' = (110) : (20\bar{1})$  and  $or' = (11\bar{1}) : (20\bar{1})$ .**

These two angles can next be found from the two right-angled triangles  $a = (100) : p = (110) : r' = (20\bar{1})$ , and  $r' = (20\bar{1}) : s' = (10\bar{1}) : o' = (11\bar{1})$ . For in the first we know the sides  $ap = 35^\circ 16'$  and  $ar' = 42^\circ 41'$ , and in the second also two sides,  $s'o' = 24^\circ 38'$  and  $r's' = 26^\circ 6'$ . From the two Napierian diagrams we have :

$$\cos pr' = \cos 42^\circ 41' \cos 35^\circ 16',$$

$$pr' = 53^\circ 7'.$$

$$\cos r'o' = \cos 24^\circ 38' \cos 26^\circ 6'.$$

$$r'o' = 35^\circ 17'.$$



These two angles  $pr'$  and  $r'o'$ , together with one other,  $po'=(110):(111)$ , make up the zone  $[r'po'r']$ , hence we can at once get the value of this third angle in the zone by difference, as follows :

$$po' = 180^\circ - (pr' + r'o') = 180^\circ - 88^\circ 24' = 91^\circ 36'.$$

The mean of the four measured values of each of these three angles on our example was almost identical with the calculated value just found, the three values being  $53^\circ 6'$ ,  $35^\circ 18'$ , and  $91^\circ 36'$ . For the whole eleven crystals the mean values were  $53^\circ 5'$ ,  $35^\circ 19'$ , and  $91^\circ 37'$ .

It is next necessary to calculate the position of the possible primary hemi-orthoprism  $s=(101)$ , and this can be done in the same manner as the complementary hemi-orthoprism  $s'=(\bar{1}01)$  was calculated, namely, by means of the anharmonic ratio of four poles in a zone.

To find  $as=(100):(101)$  and  $cs=(001):(101)$ . The four poles in question are  $a=(100)$ ,  $s=(101)$ ,  $c=(001)$ , and  $s'=(\bar{1}01)$ , and the conditions, showing the angles known, are defined in Fig. 220. The ratio is :

$$\frac{\sin s'c}{\sin s's} \cdot \frac{\sin as}{\sin ac} = \frac{\bar{1}01}{101} \cdot \frac{100}{100}$$

$$\frac{\sin s'c}{\sin s's} \cdot \frac{\sin as}{\sin ac} = \frac{\bar{1}}{2} \cdot \frac{1}{1}$$

$$\frac{\sin as}{\sin ss'} = \frac{\sin ac}{2 \sin cs'} = \tan \theta$$

$$\theta = 37^\circ 37\frac{1}{2}'$$

$$\tan \frac{1}{2}(ss' - as) = \tan \frac{1}{2}(ss' + as) \cdot \tan (45^\circ - \theta)$$

$$= \tan 55^\circ 37' \tan 7^\circ 22\frac{1}{2}'.$$

$$\frac{1}{2}(ss' - as) = 10^\circ 43'.$$

$$ss' - as = 21^\circ 26'.$$

$$ss' + as = 111^\circ 13'.$$

Hence  
and we know

By subtraction

Then

$$2as = 89^\circ 47', \text{ and consequently } as = 44^\circ 54'.$$

$$cs = ac - as = 72^\circ 54' - 44^\circ 54' = 28^\circ 0'.$$

The position of the possible pole  $s=(101)$  is thus now defined between the poles  $a=(100)$  and  $c=(001)$ .

We may next conveniently determine the position of the primary pyramid  $o=\{111\}$ .

To find  $ao=(100):(111)$  and  $oq=(111):(011)$ .

This can be done by utilising the right-angled triangle  $a=(100)$ ,  $o=(111)$ ,  $s=(101)$ , in which we know, besides the right angle at  $s$ , the angle at  $a$ , which has been shown to be  $26^\circ 11\frac{1}{2}'$ , and the side  $as=44^\circ 54'$  just calculated. From the Napierian diagram we derive :

$$\cos 26^\circ 11\frac{1}{2}' = \cot ao \tan 44^\circ 54',$$

$$\cot ao = \cos 26^\circ 11\frac{1}{2}' \cot 44^\circ 54'. \quad ao = 48^\circ 0'.$$

Then :

$$oq = aq - ao = 74^\circ 34' - 48^\circ 0' = 26^\circ 34'.$$

To find  $os=(111):(101)$  and  $ob=(111):(010)$ .

This can be done from the same triangle, and from the diagram we deduce :

$$\sin so = \sin 26^\circ 11\frac{1}{2}' \sin 48^\circ 0'. \quad so = 19^\circ 9'.$$

Then  $bo=90^\circ - so=90^\circ - 19^\circ 9' = 70^\circ 51'$ . This value is identical with the result of the only trustworthy measurement of  $bo$ .

To find  $co=(001):(111)$  and  $op=(111):(110)$ .

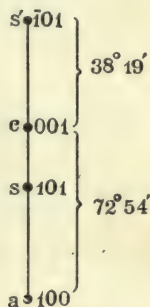


FIG. 220.

We can find  $co$  from the triangle  $cos$ , from the diagram for which by Napier's rules we have :

$$\cos co = \cos 19^\circ 9' \cos 28^\circ 0'. \quad co = 33^\circ 29'.$$

$$\text{Then} \quad op = cp - co = 76^\circ 7' - 33^\circ 29' = 42^\circ 38'.$$

The mean measured values were, for  $co$   $33^\circ 32'$ , and for  $op$   $42^\circ 35'$ .

We may next find the position of the pole  $n$ , assuming the indices to be (121), which were indicated by preliminary use of the measured angles  $bn$  and  $no$  in the anharmonic ratio of the four poles in the  $90^\circ$ -zone [ $bnos$ ]. We shall now use the reverse process to find the angles  $bn$  and  $no$ , assuming the indices. Setting forth the conditions in the usual linear diagram the ratio derived therefrom is :

$$\begin{array}{ccccccc} & & 1 & 0 & 1 & & 0 & 1 & 0 \\ & & & \times & & & \times & & \\ \sin so & \cdot & \sin bn & = & \frac{1}{1} & \frac{1}{1} & \cdot & \frac{1}{2} & \frac{1}{1} \\ \sin sn & \cdot & \sin bo & = & \frac{1}{0} & \frac{1}{1} & \cdot & \frac{0}{1} & \frac{0}{0} \\ & & & \times & & & \times & & \\ & & & 1 & 2 & 1 & & 1 & 1 & 1 \end{array}$$

$$\frac{\sin 19^\circ 9'}{\cos bn} \cdot \frac{\sin bn}{\cos 19^\circ 9'} = \frac{1}{2} \cdot \frac{1}{1} = \frac{1}{2}.$$

$$\tan bn = \frac{1}{2} \cot 19^\circ 9'. \quad bn = 55^\circ 13'.$$

$$\text{Then} \quad no = bo - bn = 70^\circ 51' - 55^\circ 13' = 15^\circ 38'.$$

To find the angles  $pn = (110) : (121)$  and  $nq = (121) : (011)$ .

This we can do from the triangle  $b = (010)$ ,  $n = (121)$ ,  $p = (110)$  in which we know the angle at  $b$ , for it is the same as the angle  $as = 44^\circ 54'$ , and the two sides including it, namely,  $bn = 55^\circ 13'$  and  $bp = 54^\circ 44'$ . Employing the formulæ ( $b$ ) on page 109 of Chapter VII. we have :

$$\tan \theta = \tan 54^\circ 44' \cos 44^\circ 54', \quad \cos pn = \frac{\cos 54^\circ 44' \cos (55^\circ 13' - \theta)}{\cos \theta}$$

$$\theta = 45^\circ 3'. \quad pn = 36^\circ 27'.$$

$$\text{Then } nq = (121) : (011) = pq - pn = 62^\circ 26' - 36^\circ 27' = 25^\circ 59'.$$

The measured values of  $pn$  and  $nq$  were respectively  $36^\circ 28'$  and  $25^\circ 58'$ , only  $1'$  different from the calculated values.

To find  $pq = (110) : (011)$ .

This angle can be most conveniently calculated by determining the two other angles in the same zone,  $sp = (101) : (110)$  and  $sq = (101) : (011)$ , which together form the supplement of  $pq$ . We can find  $sp$  from the right-angled triangle  $aps$ , and the angle  $sq$  may be similarly found from the right-angled triangle  $cqs$ . From the diagrams we at once derive :

$$\cos sp = \cos 35^\circ 16' \cos 44^\circ 54';$$

$$sp = 54^\circ 40'.$$

$$\cos sq = \cos 25^\circ 11' \cos 28^\circ 0'.$$

$$sq = 36^\circ 58'.$$

$$\text{Then } pq = 180^\circ - (54^\circ 40' + 36^\circ 58') = 88^\circ 22'.$$

The mean of the four measured values of  $pq$  on the crystal under consideration was  $88^\circ 21'$ , and the same value was obtained as the mean of the 40 measurements on the whole 11 crystals.

To find  $ps' = (110) : (10\bar{1})$  and  $qs' = (011) : (\bar{1}01)$ .

The latter can be found from the right-angled triangle  $cqs'$ , the sides  $cq$  and  $cs'$  being known. From the Napierian diagram we derive :

$$\cos qs' = \cos 25^\circ 11' \cos 38^\circ 19'. \quad qs' = 44^\circ 46'.$$

$$\text{Then } ps' = 180^\circ - (62^\circ 26' + 44^\circ 46') = 72^\circ 48'.$$

To find the positions of the prismatic forms  $p' = \{120\}$  and  $p''' = \{130\}$ .

The latter form alone has been found developed on the crystals of this salt, but the former is quite a common form on several other salts of the series (see Fig. 216a), so that it was desirable to calculate its position for purposes of comparison. Both

positions can be found from the anharmonic ratio of four poles in the right-angled zone [apb], the pole p' or p''' being the fourth pole. Drawing the usual linear diagrams, we can at once set down with their aid the ratios as follows :

$$\frac{\sin ap}{\sin ap'''} \cdot \frac{\sin bp'''}{\sin bp} = \frac{\overset{\times}{100} \cdot \overset{\times}{130}}{\overset{\times}{110} \cdot \overset{\times}{010}} = \frac{130}{110}$$
$$\frac{\sin ap}{\cos ap} \cdot \frac{\sin bp'''}{\cos bp'''} = \frac{1}{3} \cdot \frac{\bar{1}}{\bar{1}}$$
$$\tan bp''' = \frac{1}{3} \cot ap;$$
$$bp''' = 25^{\circ} 14'.$$

$$\frac{\sin ap}{\sin ap'} \cdot \frac{\sin bp'}{\sin bp} = \frac{\overset{\times}{100} \cdot \overset{\times}{120}}{\overset{\times}{110} \cdot \overset{\times}{010}} = \frac{120}{110}$$
$$\frac{\sin ap}{\cos ap} \cdot \frac{\sin bp'}{\cos bp'} = \frac{1}{2} \cdot \frac{\bar{1}}{\bar{1}}$$
$$\tan bp' = \frac{1}{2} \cot ap;$$
$$bp' = 35^{\circ} 16'.$$

Then p'''p = 54° 44' - 25° 14' = 29° 30'.      p'p = 54° 44' - 35° 16' = 19° 28'.  
The only measured values of bp''' and p'''p obtained were respectively 25° 18' and 29° 26'.

This completes the calculations of angles and elements, and it only remains now to present the summary of results.

TABLE OF RESULTS FOR AMMONIUM MAGNESIUM SULPHATE  
(NH<sub>4</sub>)<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O.

- Crystal-system :** Monoclinic. Class 5, holohedral, prismatic.  
**Habit :** Short prismatic.  
**Axial angle :** = 107° 6'.  
**Ratio of axes :** a : b : c = 0.7400 : 1 : 0.4918.  
**Forms observed :** b = {010}, c = {001}, p = {110}, p''' = {130}, q = {011}, r' = {201}, o = {111}, o' = {111}, n = {121}.

**Table of Angles :** In the table of angles which follows, the mean observed values are those derived from the whole eleven crystals included in the investigation, of which the crystal employed as an example in this chapter was the most perfect, and the mean values derived from which, where they differed at all from the mean given in the table, were even closer to the calculated values. Generally speaking, however, the mean values derived from the example are identical with those derived from the whole eleven crystals ; but the advantage of having employed also the other ten crystals lies in the fact that proof is afforded that the values derived from the example are not exceptional, but do really represent the truth as regards the angular magnitudes of this substance. The three angles used as basal angles in the calculation are marked with an asterisk.



Angle.	No. of Measure- ments.	Limits.	Mean observed.	Calculated.	Difference.
$\left\{ \begin{array}{l} ac=(100):(001) \\ as=(100):(101) \\ sc=(101):(001) \\ cr'=(001):(201) \\ cs'=(001):(\bar{1}01) \\ s'r'=(\bar{1}01):(201) \\ r'a=(201):(\bar{1}00) \\ r'c=(201):(001) \end{array} \right.$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ 13 \\ \dots \\ \dots \\ \dots \\ 12 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ 64^\circ 25' - 64^\circ 32' \\ \dots \\ \dots \\ \dots \\ 115 \ 26 - 115 \ 34 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ 64^\circ 29' \\ \dots \\ \dots \\ \dots \\ 115 \ 31 \end{array} \right\}$	$\left. \begin{array}{l} 72^\circ 54' \\ 44 \ 54 \\ 28 \ 0 \\ 64 \ 25 \\ 38 \ 19 \\ 26 \ 6 \\ 42 \ 41 \\ 115 \ 35 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ 4' \\ \dots \\ \dots \\ \dots \\ 4 \end{array} \right\}$
$\left\{ \begin{array}{l} ap=(100):(110) \\ pp'=(110):(120) \\ p'b=(120):(010) \\ pp'''=(110):(130) \\ p'''b=(130):(010) \\ pb=(110):(010) \\ pp=(110):(\bar{1}10) \end{array} \right.$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ 1 \\ 1 \\ 39 \\ 19 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ \dots \\ \dots \\ 54 \ 35 - 54 \ 50 \\ 70 \ 25 - 70 \ 46 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ 29 \ 26 \\ 25 \ 18 \\ 54 \ 44 \\ 70 \ 34 \end{array} \right\}$	$\left. \begin{array}{l} 35 \ 16 \\ 19 \ 28 \\ 35 \ 16 \\ 29 \ 30 \\ 25 \ 14 \\ * \\ 70 \ 32 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ 4 \\ 4 \\ \dots \\ 2 \end{array} \right\}$
$\left\{ \begin{array}{l} cq=(001):(011) \\ qb=(011):(010) \end{array} \right.$	$\left. \begin{array}{l} 40 \\ 40 \end{array} \right\}$	$\left. \begin{array}{l} 25 \ 4 - 25 \ 16 \\ 64 \ 43 - 64 \ 56 \end{array} \right\}$	$\left. \begin{array}{l} 25 \ 11 \\ 64 \ 49 \end{array} \right\}$	$\left. \begin{array}{l} 25 \ 11 \\ * \end{array} \right\}$	$\left. \begin{array}{l} 0 \\ \dots \end{array} \right\}$
$\left\{ \begin{array}{l} ao=(100):(111) \\ oq=(111):(011) \\ aq=(100):(011) \\ qo'=(011):(\bar{1}11) \\ o'a=(\bar{1}11):(\bar{1}00) \end{array} \right.$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ \dots \\ \dots \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ \dots \\ \dots \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ \dots \\ \dots \end{array} \right\}$	$\left. \begin{array}{l} 48 \ 0 \\ 26 \ 34 \\ 74 \ 34 \\ 34 \ 38 \\ 70 \ 48 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ \dots \\ \dots \end{array} \right\}$
$\left\{ \begin{array}{l} co=(001):(111) \\ op=(111):(110) \\ cp=(001):(110) \\ po'=(110):(\bar{1}11) \\ o'c=(111):(00\bar{1}) \\ pc=(110):(00\bar{1}) \end{array} \right.$	$\left. \begin{array}{l} 4 \\ 4 \\ 32 \\ 27 \\ 25 \\ 31 \end{array} \right\}$	$\left. \begin{array}{l} 33 \ 25 - 33 \ 39 \\ 42 \ 23 - 42 \ 43 \\ 76 \ 1 - 76 \ 17 \\ 59 \ 12 - 59 \ 24 \\ 44 \ 25 - 44 \ 43 \\ 103 \ 44 - 104 \ 2 \end{array} \right\}$	$\left. \begin{array}{l} 33 \ 32 \\ 42 \ 35 \\ 76 \ 7 \\ 59 \ 19 \\ 44 \ 34 \\ 103 \ 52 \end{array} \right\}$	$\left. \begin{array}{l} 33 \ 29 \\ 42 \ 38 \\ * \\ 59 \ 22 \\ 44 \ 31 \\ 103 \ 53 \end{array} \right\}$	$\left. \begin{array}{l} 3 \\ 3 \\ \dots \\ 3 \\ 3 \\ 1 \end{array} \right\}$
$\left\{ \begin{array}{l} bn=(010):(121) \\ no=(121):(111) \\ bo=(010):(111) \\ os=(111):(101) \end{array} \right.$	$\left. \begin{array}{l} \dots \\ \dots \\ 1 \\ \dots \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ \dots \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ 70 \ 51 \\ \dots \end{array} \right\}$	$\left. \begin{array}{l} 55 \ 13 \\ 15 \ 38 \\ 70 \ 51 \\ 19 \ 9 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ 0 \\ \dots \end{array} \right\}$
$\left\{ \begin{array}{l} bo'=(010):(\bar{1}11) \\ o's'=(\bar{1}11):(\bar{1}01) \\ o'o'=(\bar{1}11):(\bar{1}\bar{1}\bar{1}) \end{array} \right.$	$\left. \begin{array}{l} 7 \\ \dots \\ 3 \end{array} \right\}$	$\left. \begin{array}{l} 65 \ 19 - 65 \ 28 \\ \dots \\ 49 \ 9 - 49 \ 21 \end{array} \right\}$	$\left. \begin{array}{l} 65 \ 22 \\ \dots \\ 49 \ 16 \end{array} \right\}$	$\left. \begin{array}{l} 65 \ 22 \\ 24 \ 38 \\ 49 \ 16 \end{array} \right\}$	$\left. \begin{array}{l} 0 \\ \dots \\ 0 \end{array} \right\}$
$\left\{ \begin{array}{l} sq=(101):(011) \\ qp=(011):(\bar{1}10) \\ ps=(\bar{1}10):(\bar{1}01) \\ pq=(\bar{1}10):(0\bar{1}\bar{1}) \end{array} \right.$	$\left. \begin{array}{l} \dots \\ 40 \\ \dots \\ 40 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ 88 \ 11 - 88 \ 29 \\ \dots \\ 91 \ 33 - 91 \ 49 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ 88 \ 21 \\ \dots \\ 91 \ 39 \end{array} \right\}$	$\left. \begin{array}{l} 36 \ 58 \\ 88 \ 22 \\ 54 \ 40 \\ 91 \ 38 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ 1 \\ \dots \\ 1 \end{array} \right\}$
$\left\{ \begin{array}{l} s'q=(\bar{1}01):(011) \\ qn=(011):(121) \\ np=(121):(110) \\ qp=(011):(110) \\ ps'=(110):(10\bar{1}) \\ pq=(110):(0\bar{1}\bar{1}) \end{array} \right.$	$\left. \begin{array}{l} \dots \\ 1 \\ 1 \\ 40 \\ \dots \\ 40 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ \dots \\ \dots \\ 62 \ 18 - 62 \ 38 \\ \dots \\ 117 \ 23 - 117 \ 44 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ 25 \ 58 \\ 36 \ 28 \\ 62 \ 26 \\ \dots \\ 117 \ 34 \end{array} \right\}$	$\left. \begin{array}{l} 44 \ 46 \\ 25 \ 59 \\ 36 \ 27 \\ 62 \ 26 \\ 72 \ 48 \\ 117 \ 34 \end{array} \right\}$	$\left. \begin{array}{l} \dots \\ 1 \\ 1 \\ 0 \\ \dots \\ 0 \end{array} \right\}$
$\left\{ \begin{array}{l} r'o'=(201):(\bar{1}11) \\ o'p=(\bar{1}11):(110) \\ pr'=(110):(20\bar{1}) \\ r'p=(201):(110) \end{array} \right.$	$\left. \begin{array}{l} 27 \\ 28 \\ 33 \\ 32 \end{array} \right\}$	$\left. \begin{array}{l} 35 \ 11 - 35 \ 28 \\ 91 \ 28 - 91 \ 43 \\ 52 \ 53 - 53 \ 14 \\ 126 \ 45 - 127 \ 5 \end{array} \right\}$	$\left. \begin{array}{l} 35 \ 19 \\ 91 \ 37 \\ 53 \ 5 \\ 126 \ 55 \end{array} \right\}$	$\left. \begin{array}{l} 35 \ 17 \\ 91 \ 36 \\ 53 \ 7 \\ 126 \ 53 \end{array} \right\}$	$\left. \begin{array}{l} 2 \\ 1 \\ 2 \\ 2 \end{array} \right\}$

Total number of measurements: 581.

This table embodies over a hundred further measurements, on the same eleven crystals, than were given in the author's memoir in the *Journal of the Chemical Society* for 1905, pages 1134-35, of the angles  $po'$  and  $o'c$ , and  $r'o'$  and  $o'p$ . Also the angles in the zone  $[bno]$  have been revised, only one measured value in this zone, that of the angle  $bo$ , having been found sufficiently trustworthy, owing to the poor quality of the images from the  $n$ -faces when adjusted in this zone, as compared with their much clearer images when adjusted in the zone  $[s'qnp]$ .

The general close agreement of the observed and calculated values, the maximum difference being only  $4'$ , may be taken as evidence both of accurate measurement and correct calculation.

## CHAPTER XVIII

### TRICLINIC OR ANORTHIC SYSTEM

Three unequal crystallographic axes all inclined to each other at angles other than  $90^\circ$ . Characterised by no symmetry at all or only centro-symmetry.

THERE can obviously be only two classes of symmetry fulfilling these conditions, namely, one, class 2, in which there is centro-symmetry, and another, class 1, in which there is not. The stereographic projections of the two are given in Fig. 221 (class 1) and Fig. 222 (class 2). Each

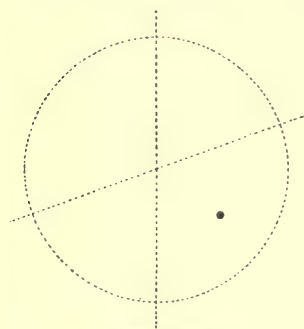


FIG. 221.—Class 1.

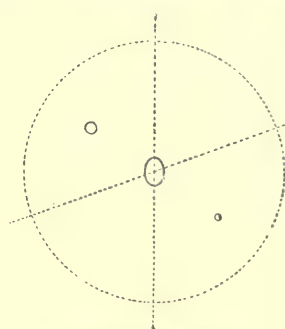


FIG. 222.—Class 2.

face in class 1 is a separate form, hence one pole only is shown in Fig. 221 as representative of  $\{hkl\}$ . In class 2 each form consists of a pair of parallel faces, so that one pole appears in each hemisphere in Fig. 222. In the triclinic

system the ordinary mode of projection is reverted to, the axes shown in dotted lines being the  $a$  and  $b$  axes, the plane of these axes being the plane of projection; the monoclinic system is alone exceptional in having the axial plane  $ac$  as the plane of projection.

*Class 2.—Triclinic-Pinakoidal or Holohedral Class. Type, Centro-Symmetrical or Digonal Alternating.*

The nature of the symmetry of this holohedral class of the triclinic system indicated in stereographic projection in Fig. 222, has already been fully discussed in Chapter IX. and illustrated in Fig. 76, p. 134, as it forms the first of the three cases of alternating symmetry there analysed. It was clearly shown that the centro-symmetry, which has hitherto been regarded as the only symmetry present in the class, is really the effect in



a specific case of the simultaneous operation of a plane of compound or reflection-symmetry and of a digonal axis perpendicular thereto. Similar cases of rotation about an axis and simultaneous reflection over a plane were investigated for tetragonal and hexagonal axes, and shown to lead to a similar result in the case of a hexagonal axis, centro-symmetry being again the accompaniment; while the tetragonal case did not lead to centro-symmetry at all, and the trigonal case also referred to was shown to be from its very nature an impossible one. Hence, while we may equally correctly describe the symmetry of this class 2 as being either "centro-symmetrical" or "digonal alternating," it must be remembered that the centre of symmetry is not a true element of symmetry, but merely the accompaniment, in this case as in the hexagonal case, of a reflection over a plane, simultaneously with a rotation about an axis.

The result of the presence of nothing but centro-symmetry is that the whole of the forms of this holohedral class of the triclinic system consist in each case of two parallel faces only, one on each side of the centre, hence the class is called "pinakoidal." It is scarcely convenient for the purposes of ready identification to term them all merely pinakoids of various orders, in accordance with the scheme of Fedorov, but better to retain also the nomenclature of the orthorhombic system, in conjunction with the word "pinakoid," in labelling the seven specific types of forms. If the order of the pinakoid be given in addition to this, the advantages of both the new and the older familiar nomenclature are combined.

Three well-developed faces, which exhibit mutual inclinations as near  $90^\circ$  as possible, are chosen from the most prominent faces developed on the crystal, as the directions of the axial planes and for the fundamental pinakoid faces (100), (010), and (001), and their edges of intersection as the directions of the three crystallographic axes. The closed doubly-oblique prismatic six-faced solid formed by these three faces and their parallel fellows, shown in Fig. 223, may be regarded as a rectangular orthorhombic prism closed by basal plane, which has been subjected to deformation in two directions, and thus converted into a parallelepipedon with the same edges but now inclined at angles other than  $90^\circ$ .

A fourth prominent face inclined to all three axial planes, that is, replacing a solid angle (see Fig. 40, p. 72, Chapter V., the face *o*), is next chosen as the primary parametral plane (111), determining the relative lengths of the axes, which in general will always be unequal (for if all three or any two were equal, by chance, at any particular temperature, the slightest change in the temperature would produce inequality, the thermal and other physical properties varying with the direction in the crystal). Failing the presence of such a plane, the axial lengths may be fixed by means of two faces each of which is inclined to two of the axes, that is, each of which replaces an edge of the fundamental doubly-oblique prism.

Maintaining the analogy of the orthorhombic nomenclature, the pair of faces intersected by the axis chosen as the vertical one *c*, but parallel to the two other axes,

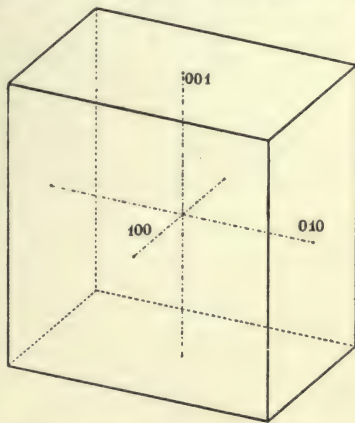


FIG. 223.—Triclinic Prism, formed by the three Primary Pinakoids.

may be termed the **basal pinakoid**, or **third pinakoid**, their indices being  $\{001\}$  and  $\{00\bar{1}\}$  and the form symbol  $\{001\}$ . The longer of the two other axes is arranged laterally right-and-left and made the  $b$  axis; it is termed the macro-diagonal, and the pair of faces parallel to it and to the vertical axis, but intersected by the shorter front-and-back axis  $a$ , the brachy-diagonal, are called the **macro-pinakoid** or **first pinakoid**. Their indices are  $\{100\}$  and  $\{\bar{1}00\}$ , and the form symbol is  $\{100\}$ . Similarly, the pair of faces parallel to the brachy-diagonal and to the vertical axis  $c$ , but intersected by the macro-diagonal, the lateral axis  $b$ , are named the **brachy-pinakoid** or **second pinakoid**, their indices being  $\{010\}$  and  $\{0\bar{1}0\}$ , and the form symbol  $\{010\}$ .

Other forms parallel to the vertical axis,  $\{h k 0\}$ , may analogously be termed **prismatic pinakoids**, or pinakoids of the third order, two such complementary forms  $\{h k 0\}$  and  $\{h \bar{k} 0\}$  being together the doubly-oblique equivalent of an orthorhombic prism.

Forms parallel to the macro-diagonal  $\{h 0 l\}$ , are **macro-domal pinakoids** or pinakoids of the second order, two complementary ones  $\{h 0 l\}$  and  $\{\bar{h} 0 l\}$  being together analogous to the orthorhombic macro-domal prism.

Forms parallel to the brachy-diagonal  $\{0 k l\}$  and  $\{0 \bar{k} l\}$  are similarly **brachy-domal pinakoids**, or pinakoids of the first order.

The general form  $\{h k l\}$  intersected by all three axes is still by analogy termed pyramidal, although it takes four such forms to make up the equivalent of the rhombic

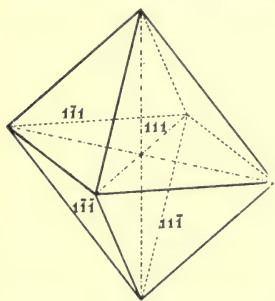
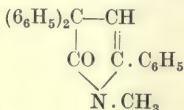


FIG. 224.—Triclinic Bipyramid, formed by four primary fourth order Pinakoids.

bipyramid, as shown in Fig. 224, namely,  $\{h k l\}$  consisting of the faces  $(h k l)$  and  $(\bar{h} \bar{k} \bar{l})$ ,  $\{\bar{h} k l\}$  made up of  $(\bar{h} k l)$  and  $(h \bar{k} \bar{l})$ ,  $\{h \bar{k} l\}$  consisting of  $(h \bar{k} l)$  and  $(\bar{h} k \bar{l})$ , and  $\{\bar{h} \bar{k} l\}$  composed of  $(\bar{h} \bar{k} l)$  and  $(h k \bar{l})$ . Each form may be most fittingly described as **bipyramidal-pinakoidal**, or as a pinakoid of the fourth order, that is, not parallel to any of the three axes; the former term may be taken as indicating that while each form consists of only a pair of parallel faces the *tout ensemble* of the faces having similar index numbers makes up a triclinic bipyramid. This latter solid was formerly known as a "doubly-oblique rhombic pyramid." Its primary representative is shown in Fig. 224. The only other term which expresses the nature of these bipyramidal-pinakoids is "tetarto-bipyramid," but this term is unsuitable, as it would appear to indicate a tetartohedral type of form, whereas these pinakoids are fully holohedral or holosymmetric, that is to say, they exhibit the whole symmetry (such as it is, being only centro-symmetry) of the system.

The parametral face  $(111)$  chosen to determine the lengths of the axes is one of the two faces of the first primary bipyramidal-pinakoid. The pole shown in the upper hemisphere (the solid dot) in Fig. 222 is that of the  $(111)$  face of a real triclinic crystal measured by the author, of the substance methyl triphenylpyrrholone. The actual crystal is shown in Fig. 47 and its stereographic projection in Fig. 48, p. 98. It is a particularly characteristic example of a triclinic crystal fairly rich in faces. The ratio of the axes is  $a:b:c=0.9059:1:0.8695$ ; the axial angles are  $\alpha=79^\circ 52'$ ,  $\beta=86^\circ 3'$ , and  $\gamma=70^\circ 26'$ . The forms developed are:  $a=\{100\}$ ,  $b=\{010\}$ ,  $c=\{001\}$ ,  $p=\{110\}$ ,  $p'=\{1\bar{1}0\}$ ,  $o=\{111\}$ ,  $r=\{1\bar{1}1\}$ ,  $o'=\{\bar{1}11\}$ ,  $s=\{\bar{1}\bar{1}1\}$ ,  $m=\{101\}$ ,  $n=\{10\bar{1}\}$ ,  $q=\{011\}$ ,  $q'=\{0\bar{1}1\}$ , and  $r'=\{112\}$ .



*List of Forms in Class 2, each of 2 Faces.*

- $\{001\}$  Basal pinakoid or third pinakoid.
- $\{100\}$  Macro-pinakoid or first pinakoid.
- $\{010\}$  Brachy-pinakoid or second pinakoid.

- $\{hk0\}$  and  $\{h\bar{k}0\}$  Prismatic pinakoids or pinakoids of the third order, including the primary  $\{110\}$  and  $\{1\bar{1}0\}$ .
- $\{h0l\}$  and  $\{h\bar{0}l\}$  Macro-domal pinakoids or pinakoids of the second order, including the primary ones  $\{101\}$  and  $\{1\bar{1}01\}$ .
- $\{0kl\}$  and  $\{0\bar{k}l\}$  Brachy-domal pinakoids or pinakoids of the first order, including the primary ones  $\{011\}$  and  $\{0\bar{1}1\}$ .
- $\{hkl\}$ ,  $\{h\bar{k}l\}$ ,  $\{h\bar{k}\bar{l}\}$ , and  $\{h\bar{k}l\}$  Bipyramidal pinakoids or pinakoids of the fourth order, including the primary ones  $\{111\}$  (parametral),  $\{1\bar{1}1\}$ ,  $\{1\bar{1}\bar{1}\}$ , and  $\{11\bar{1}\}$ .

It will be observed that the whole of the forms in this list are represented by their primary representatives on the crystal of methyl triphenylpyrrholone, Fig. 47, hence its peculiar suitability as an example of triclinic symmetry.

Copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , is one of the best-known examples of holohedral triclinic symmetry, and a crystal of this salt will be worked through in detail in the next chapter, and all its elements found by calculation from direct measurements of the interfacial angles.

*Class 1.—Asymmetric Class. No Symmetry. Triclinic-Hemihedral Class. Type, Pedial.*

This class, represented in stereographic projection in Fig. 225, has the unique distinction of exhibiting no symmetry whatever. It merely obeys the fundamental crystallographic law of rational indices.

Every face developed on the crystal is a separate form, a pedion (from  $\pi\epsilon\delta\iota\omicron\nu$ , a plane), hence the character of this class is pedial, just as that of class 2 is pinakoidal. Sometimes, however, two parallel faces are developed on crystals of class 1, and this may happen as regards several, or even all, of the forms present, so that on preliminary inspection it may appear to belong to the holohedral class 2 just referred to. But closer examination will reveal the fact that the two faces of each parallel pair are of unequal brilliancy, or exhibit different markings, or afford different etched figures with solvents, which distinguish each face as a separate form. Moreover,

it is an interesting fact, which has doubtless to do with the most favourable conditions for the simultaneous growth of the various faces, that both the complementary forms, that is, the two faces which in class 2 make up a single form, are more frequently found simultaneously developed when the indices are low numbers, than when they are more complicated. Hence, we most frequently find the complementary primary forms both present, while in the cases of forms with higher indices, the higher the latter are, the more likely are we to find only a single face-form represented, its parallel face-form being absent. Such a fact alone is of great value in enabling a decision to be arrived at as to whether a crystal belongs to class 1 or to class 2, and the conclusion can be confirmed by etched-figure tests with a minute quantity of a solvent.

The nomenclature of these pedial forms of class 1 is a somewhat difficult matter, there being two courses open, neither of which in the author's opinion is alone satisfactory, but which together are fully so. The first possibility is to retain the

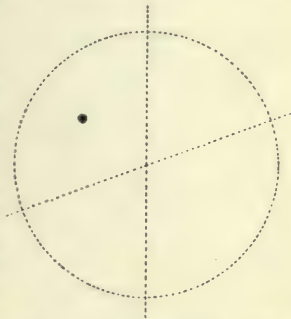


FIG. 225.—General Form of Class 1 (no Symmetry).





each face on the crystal is a separate form, the indices of the back faces are inserted in the drawing, in broken figures, as well as those of the front faces (continuous figures).

The ratio of the axes is:  $a:b:c=0.7847:1:1.5179$ ; and the three axial angles are:  $\alpha=72^\circ 24'$ ,  $\beta=98^\circ 32'$ ,  $\gamma=92^\circ 40'$ , referring, as usual for triclinic crystals in this book, to the axial angles in the right-front-upper octant.

## CHAPTER XIX

### PRACTICAL EXAMPLE OF A TRICLINIC CRYSTAL

#### Copper Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

##### *Class 2.*

SULPHATE of copper is well known to crystallise from its solution in water in magnificent blue crystals, commonly termed "blue vitriol," which contain five molecules of water of crystallisation. These crystals belong to the holohedral class (class 2) of the triclinic system, and as they are so easily procurable, by the simple evaporation of only very slightly supersaturated solutions, in adequately perfect form for measurement, they afford perhaps the best example of triclinic symmetry that could be chosen for the purposes of this book. Although the substance is so cheap and common, it is somewhat singular that the literature concerning the crystallography of copper sulphate is in a most unsatisfactory state. The hitherto accepted elements and angles of the crystals are those of Kupffer,<sup>1</sup> made in the year 1826. These are quoted at some length by Rammelsberg in his *Krystallographisch-physikalischen Chemie*, but the values and their order are quite different in the earlier 1855 edition from those given in the later 1881 edition. In fact the values given by Kupffer, and quoted by Rammelsberg, are so confused, the acute and obtuse angles being almost inextricably mixed up, that a reinvestigation of the crystals of the salt was imperative. The values of Kupffer quoted by von Groth in his *Physikalische Krystallographie* as late as the third, 1895, edition, include the following for the elements :

$$a : b : c = 0.5656 : 1 : 0.5499 ; \alpha = 97^\circ 39', \beta = 106^\circ 49', \gamma = 77^\circ 37'.$$

Now it will be shown in this chapter that if the axial ratio just quoted be approximately correct, then the values for  $\alpha$  and  $\gamma$  are the supplements of the true values, while the  $\beta$  value is correctly given. In the fourth, 1905, edition, and also in his *Chemische Krystallographie* (vol. ii. 1908, p. 419), von Groth corrects this inversion and gives the following altogether revised elements, derived from unpublished measurements made by T. V. Barker in his (von Groth's) laboratory at Munich :

$$a : b : c = 0.5721 : 1 : 0.5554 ; \alpha = 82^\circ 5', \beta = 107^\circ 8', \gamma = 102^\circ 41'.$$

<sup>1</sup> *Pogg. Ann.*, 1826, 8, 217.



The measurements on which these elements were based remain as yet unpublished, and the author has, therefore, felt it incumbent to carry out a complete morphological investigation of the crystals of copper sulphate, and its results are embodied in this chapter, and are expressed in concrete form in those derived from the particularly excellent crystal chosen as the typical example of a triclinic crystal. They agree quite well with the elements of Barker, so that it is certain that he and the author are unanimous as to the mode of setting up the crystal and the disposition of the axes, a conclusion which has been further confirmed by a friendly communication from Mr. Barker.

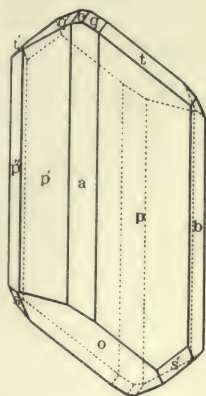


FIG. 227.  
Measured Crystal of Copper Sulphate.

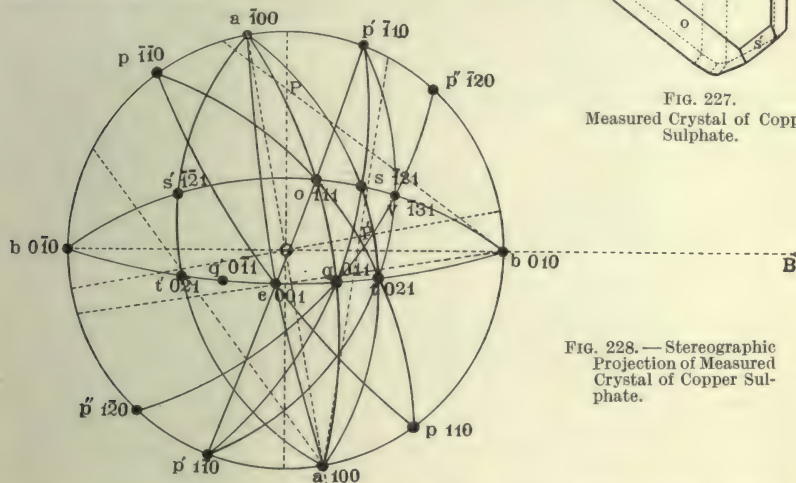


FIG. 228. — Stereographic Projection of Measured Crystal of Copper Sulphate.

A dozen crystals of were selected from among different crops, and the the present example. It the construction of which will XXV. and is shown in jectioin is given in Fig. will be described later in examined presented one the same zone,  $[apb]$  in a prismatic one, that is, development a prismatic the relative development in different crops. The from which this example was selected were characterised by pre-dominantly developed  $o$ -faces; indeed in the cases of some of them

the highest obtainable perfection the best afforded by numerous best of all is the one chosen as is represented in Fig. 227, the be fully described in Chapter Fig. 359. Its stereographic pro-228, the construction of which this chapter. All the crystals property in common, namely, that Fig. 227, was always markedly it conferred by its elongated habit on the crystal, although of the end-faces was very different crystals of the particular crop

this face appeared at first sight to be the only one at each end, although examination with a lens revealed smaller ones.

The prismatically developed zone is arranged for descriptive purposes vertically, that is, its zone-axis is chosen as the direction of the vertical axis  $c$ . The two faces in it marked respectively  $a$  and  $b$  and their parallel fellows are chosen as the pinakoids  $\{100\}$  and  $\{010\}$ ; the two parallel  $a$ -faces are not so broad as the two  $b$ -faces. The intermediate broader faces on each side of  $a$ , which cause more or less flattening of the prism, are considered as the two primary-prism forms  $p = \{110\}$  and  $p' = \{1\bar{1}0\}$ , each consisting of a pair of parallel faces. In addition, the prism zone also includes a pair of parallel faces  $p''$  of the form  $\{1\bar{2}0\}$ . The stereographic projection is so arranged that this prism zone affords the primitive circle, that is, its zone plane is the plane of projection.

The mode of measuring a crystal has now been so thoroughly dealt with in the examples taken in previous chapters to illustrate the other crystal-systems, that we may here pass on to give at once a concise record of the measurements obtained with the various zones on this typical triclinic crystal. The relation of the zones to each other will be obvious from the drawing of the crystal in Fig. 227 and its stereographic projection in Fig. 228.

#### THE PRISM ZONE.

Circle Readings.	Angles.
$\left\{ \begin{array}{l} p \quad 360^\circ \quad 0'A \\ b \quad 306 \quad 56 \text{ A} \\ p'' \quad 259 \quad 36 \\ p' \quad 237 \quad 4 \text{ A} \\ a \quad 205 \quad 56 \\ p \quad 179 \quad 55 \text{ A} \\ b \quad 126 \quad 55 \\ p'' \quad 79 \quad 45 \\ p' \quad 57 \quad 9 \text{ A} \\ a \quad 26 \quad 3 \\ p \quad 0 \quad 0 \text{ A} \end{array} \right.$	$\left. \begin{array}{l} pb \quad 53^\circ \quad 4'A \\ bp'' \quad 47 \quad 20 \\ p''p' \quad 22 \quad 32 \text{ f} \\ p'a \quad 31 \quad 8 \\ ap \quad 26 \quad 1 \text{ f} \\ pb \quad 53 \quad 0 \\ bp'' \quad 47 \quad 10 \\ p''p' \quad 22 \quad 36 \text{ f} \\ p'a \quad 31 \quad 6 \\ ap \quad 26 \quad 3 \text{ f} \end{array} \right\} \begin{array}{l} bp' \quad 69^\circ \quad 52' \\ p'p \quad 57 \quad 9 \text{ A} \\ ab \quad 79 \quad 1 \\ bp' \quad 69 \quad 46 \\ p'p \quad 57 \quad 9 \text{ A} \\ ab \quad 79 \quad 7 \end{array}$

#### ZONE $[bc]$ .

Circle Readings.	Angles.
$\left\{ \begin{array}{l} b \quad 360^\circ \quad 0'A \\ t \quad 315 \quad 35 \text{ A} \\ q \quad 295 \quad 21 \text{ A} \\ c \quad 265 \quad 43 \\ q' \quad 238 \quad 12 \\ t' \quad 220 \quad 47 \\ b \quad 180 \quad 0 \text{ A} \\ t \quad 135 \quad 30 \text{ A} \\ q \quad 115 \quad 14 \\ c \quad 85 \quad 37 \\ q' \quad 58 \quad 7 \\ t' \quad 40 \quad 34 \\ b \quad 0 \quad 0 \text{ A} \end{array} \right.$	$\left. \begin{array}{l} bt \quad 44^\circ \quad 25'A \\ tq \quad 20 \quad 14 \text{ A} \\ qc \quad 29 \quad 38 \\ cq' \quad 27 \quad 31 \\ q't' \quad 17 \quad 25 \\ t'b \quad 40 \quad 47 \\ bt \quad 44 \quad 30 \text{ A} \\ tq \quad 20 \quad 16 \\ qc \quad 29 \quad 37 \\ cq' \quad 27 \quad 30 \\ q't' \quad 17 \quad 33 \\ t'b \quad 40 \quad 34 \end{array} \right\} \begin{array}{l} bq \quad 64^\circ \quad 39'A \\ qq' \quad 57 \quad 9 \\ q'b \quad 58 \quad 12 \\ bq \quad 64 \quad 46 \\ qq' \quad 57 \quad 7 \\ q'b \quad 58 \quad 7 \end{array} \left. \begin{array}{l} bc \quad 94^\circ \quad 17' \\ bc \quad 94 \quad 23 \end{array} \right\}$

Circle Readings.			Angles.		
Zone [aoq].					
$\left\{ \begin{array}{l} a \\ o \\ q \end{array} \right.$	$\left\{ \begin{array}{l} 360^\circ \\ 300 \\ 249 \end{array} \right.$	$\left\{ \begin{array}{l} 0^\circ \text{ A} \\ 25 \text{ A} \\ 43 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} ao \\ oq \\ qa \end{array} \right.$	$\left\{ \begin{array}{l} 59^\circ \\ 50 \\ 69 \end{array} \right.$	$\left\{ \begin{array}{l} 35^\circ \text{ A} \\ 42 \text{ A} \\ 43 \end{array} \right.$
$\left\{ \begin{array}{l} a \\ o \\ q \end{array} \right.$	$\left\{ \begin{array}{l} 180 \\ 120 \\ 69 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 23 \text{ A} \\ 43 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} ao \\ oq \\ qa \end{array} \right.$	$\left\{ \begin{array}{l} 59^\circ \\ 50 \\ 69 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \\ 40 \text{ A} \\ 43 \text{ A} \end{array} \right.$
$\left\{ \begin{array}{l} a \\ o \\ q \end{array} \right.$	$\left\{ \begin{array}{l} 180 \\ 120 \\ 69 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 23 \text{ A} \\ 43 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} ao \\ oq \\ qa \end{array} \right.$	$\left\{ \begin{array}{l} 59^\circ \\ 50 \\ 69 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \\ 40 \text{ A} \\ 43 \text{ A} \end{array} \right.$
Zone [at's].					
$\left\{ \begin{array}{l} a \\ t' \\ s' \end{array} \right.$	$\left\{ \begin{array}{l} 360^\circ \\ 272 \\ 238 \end{array} \right.$	$\left\{ \begin{array}{l} 0' \\ 45 \text{ A} \\ 59 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} at' \\ t's' \\ s'a \end{array} \right.$	$\left\{ \begin{array}{l} 87^\circ \\ 33 \\ 58 \end{array} \right.$	$\left\{ \begin{array}{l} 15' \\ 46 \text{ A} \\ 59 \end{array} \right.$
$\left\{ \begin{array}{l} a \\ t' \\ s' \end{array} \right.$	$\left\{ \begin{array}{l} 180 \\ 92 \\ 59 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 49 \text{ A} \\ 8 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} at' \\ t's' \\ s'a \end{array} \right.$	$\left\{ \begin{array}{l} 87^\circ \\ 33 \\ 59 \end{array} \right.$	$\left\{ \begin{array}{l} 11' \\ 41 \text{ A} \\ 8 \end{array} \right.$
$\left\{ \begin{array}{l} a \\ t' \\ s' \end{array} \right.$	$\left\{ \begin{array}{l} 180 \\ 92 \\ 59 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 49 \text{ A} \\ 8 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} at' \\ t's' \\ s'a \end{array} \right.$	$\left\{ \begin{array}{l} 87^\circ \\ 33 \\ 59 \end{array} \right.$	$\left\{ \begin{array}{l} 11' \\ 41 \text{ A} \\ 8 \end{array} \right.$
Zone [pot].					
$\left\{ \begin{array}{l} p \\ o \\ t \end{array} \right.$	$\left\{ \begin{array}{l} 360^\circ \\ 287 \\ 233 \end{array} \right.$	$\left\{ \begin{array}{l} 0' \\ 58 \text{ A} \\ 29 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} po \\ ot \\ tp \end{array} \right.$	$\left\{ \begin{array}{l} 72^\circ \\ 54 \\ 53 \end{array} \right.$	$\left\{ \begin{array}{l} 2' \\ 29 \text{ A} \\ 31 \text{ A} \end{array} \right.$
$\left\{ \begin{array}{l} p \\ o \\ t \end{array} \right.$	$\left\{ \begin{array}{l} 179 \\ 107 \\ 53 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \text{ A} \\ 58 \text{ A} \\ 23 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} po \\ ot \\ tp \end{array} \right.$	$\left\{ \begin{array}{l} 72^\circ \\ 54 \\ 53 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \text{ A} \\ 35 \text{ A} \\ 23 \end{array} \right.$
$\left\{ \begin{array}{l} p \\ o \\ t \end{array} \right.$	$\left\{ \begin{array}{l} 179 \\ 107 \\ 53 \end{array} \right.$	$\left\{ \begin{array}{l} 58 \text{ A} \\ 58 \text{ A} \\ 23 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} po \\ ot \\ tp \end{array} \right.$	$\left\{ \begin{array}{l} 72^\circ \\ 54 \\ 53 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \text{ A} \\ 35 \text{ A} \\ 23 \end{array} \right.$
Zone [ast].					
$\left\{ \begin{array}{l} a \\ s \\ t \end{array} \right.$	$\left\{ \begin{array}{l} 360^\circ \\ 290 \\ 250 \end{array} \right.$	$\left\{ \begin{array}{l} 0' \\ 47 \\ 9 \end{array} \right.$	$\left\{ \begin{array}{l} as \\ st \\ ta \end{array} \right.$	$\left\{ \begin{array}{l} 69^\circ \\ 40 \\ 70 \end{array} \right.$	$\left\{ \begin{array}{l} 13' \\ 38 \\ 9 \end{array} \right.$
$\left\{ \begin{array}{l} a \\ s \\ t \end{array} \right.$	$\left\{ \begin{array}{l} 180 \\ 110 \\ 70 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 42 \\ 6 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} as \\ st \\ ta \end{array} \right.$	$\left\{ \begin{array}{l} 69^\circ \\ 40 \\ 70 \end{array} \right.$	$\left\{ \begin{array}{l} 18 \\ 36 \\ 6 \end{array} \right.$
$\left\{ \begin{array}{l} a \\ s \\ t \end{array} \right.$	$\left\{ \begin{array}{l} 180 \\ 110 \\ 70 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 42 \\ 6 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} as \\ st \\ ta \end{array} \right.$	$\left\{ \begin{array}{l} 69^\circ \\ 40 \\ 70 \end{array} \right.$	$\left\{ \begin{array}{l} 18 \\ 36 \\ 6 \end{array} \right.$
Zone [bs'o].					
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 360^\circ \\ 319 \\ 256 \end{array} \right.$	$\left\{ \begin{array}{l} 0^\circ \text{ A} \\ 8 \text{ A} \\ 24 \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 234 \\ 220 \\ 180 \end{array} \right.$	$\left\{ \begin{array}{l} 37 \text{ A} \\ 22 \\ 0 \end{array} \right.$	$\left\{ \begin{array}{l} sv \\ vb \\ bs' \end{array} \right.$	$\left\{ \begin{array}{l} 14 \\ 40 \\ 40 \end{array} \right.$	$\left\{ \begin{array}{l} 15 \\ 22 \\ 52 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 8 \text{ A} \\ 19 \text{ A} \\ 39 \text{ A} \end{array} \right.$	$\left\{ \begin{array}{l} bs' \\ s'o \\ os \end{array} \right.$	$\left\{ \begin{array}{l} 40^\circ \\ 62 \\ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 52^\circ \text{ A} \\ 44 \\ 47 \end{array} \right.$
$\left\{ \begin{array}{l} b \\ s' \\ o \end{array} \right.$	$\left\{ \begin{array}{l} 139 \\ 76 \\ 54 \end{array} \right.</$				

The two faces of the basal pinakoid  $c = \{001\}$  were so small and poorly reflecting that a satisfactory adjustment of the zone  $[ac]$ , in which no other faces besides  $a$  and  $c$  were present, was not possible, and consequently trustworthy measurements of the angle  $ac$  were not obtained. As the zone  $[bc]$  did not depend for its adjustment on the  $c$ -faces, excellent other faces being present, reliable measurements were obtained for the angles involving  $c$  in that zone. The faces of all forms other than  $c$  afforded excellent reflections, the chosen crystal being almost free from striation, so common in the prism zone of copper sulphate.

In order to assist in following the relationship of these several zones an approximate stereographic projection had been constructed, but having now completed the measurements we are in a position to construct it accurately. The procedure for the construction of the projection for a triclinic crystal, which is the most general case that could be proposed owing to the entire absence of right angles, has been clearly set forth in Chapter VI., and an example there given. We shall proceed, therefore, on those lines.

We first draw the primitive circle. Its radius in the author's original drawing, from which Fig. 228 was reproduced approximately half-size, was 55 millimetres. The brachy-pinakoid poles  $b = (010)$  and  $b = (0\bar{1}0)$  are inserted at the extremities of the horizontal diameter, which latter, however, should only be drawn in dotted line, as it is not the great circle of a zone, all the zones being obliquely inclined to each other. The poles of the succeeding faces in the prism zone,  $p$ ,  $a$ ,  $p'$ , and  $p''$ , are next inserted at their proper angular distances around the primitive circle, as indicated by the



prism-zone measurements. We have next to find the position of some pole situated not far from the centre, in order to be able to proceed to other zones. Usually the basal pinakoid  $c=(001)$  is the most convenient pole to find as it fulfils the *desideratum* of being near the centre, and is obviously the representative in the triclinic system of the basal plane which in the rectangular systems is situated at the centre itself. That course has been pursued in the example, methyl triphenylpyrrolone, worked out in Chapter VI. But in the case of copper sulphate it has just been pointed out that a satisfactory measurement of the primary angle between  $a=(100)$  and  $c=(001)$  was impossible. We shall subsequently show how the angle can be calculated from other trustworthy measurements, but we have not yet proceeded to the description of the calculations. Moreover, the angle  $bc$ , of which good measurements were obtained, and which would be the other angle required to enable us to fix the position of the pole  $c=(001)$ , is greater than  $90^\circ$ , namely,  $94^\circ 20'$ , and is not, therefore, quite so convenient for the purposes of the calculation of the point B and the radius Bc by the simple formulæ of pages 98 and 99, Chapter VI. We shall, therefore, choose the pole  $q=(011)$  as the more convenient one for determination.

Following the instructions given in Chapter VI., we have the following data :

$$r = 55 \text{ mm.} ; \theta = aq = 69^\circ 43' ; \phi = bq = 64^\circ 43'.$$

We then draw the produced radii OA and OB through O and  $a=(100)$  and through O and  $b=(010)$ , such that

$$OA = \frac{r}{\cos \theta} = 158.7, \text{ and } OB = \frac{r}{\cos \phi} = 128.8.$$

Having thus found the points A and B, the calculated distances OA and OB being in millimetres, we next find the radii Aq and Bq of two little arcs, constructed from A and B as centres, which intersect at q and thus define the position of that pole.

By the formulæ of Chapter VI.,

$$Aq - r \tan \theta = 148.8, \text{ and } Bq = r \tan \phi = 116.4.$$

We then draw the two little arcs, with radius Aq (in millimetres) from A and with radius Bq from B, and insert the pole  $q=(011)$  at their point of intersection.

We have then three points  $b=(010)$ ,  $q=(011)$ , and  $b=(0\bar{1}0)$  on the zone  $[bqc]$ , and can at once construct the zonal arc by the usual method of drawing a circular arc to pass through three points. The other poles in the zone,  $t=(021)$ ,  $c=(001)$ ,  $q'=(0\bar{1}1)$ , and  $t'=(0\bar{2}1)$  are then to be inserted at their proper positions corresponding to the measured angles. In order to do this, we first find the pole of the zone, by joining  $b=(010)$  to the point of intersection of the zone circle with the vertical diameter (drawn in dotted line exactly at right angles to the diameter  $bb$ ) and producing the line till it cuts the primitive circle, then marking off another point on that circle  $90^\circ$  from this, and joining this last point to  $b=(010)$ . Where this line cuts the vertical diameter is the zonal pole P required. To find the positions of  $t$ ,  $q$ ,  $c$ ,  $q'$ , and  $t'$  we mark off the observed angles along the lower half of the primitive circle, and join the points thus marked off to the pole P; these lines will cut the zonal arc at the facial poles required.

We can next draw zonal arcs terminating at  $a=(100)$  and its parallel fellow  $a=(\bar{1}00)$  to pass through  $t$ ,  $q$ ,  $c$ ,  $q'$ , and  $t'$ , respectively as a third point. Only one further piece of construction is then needed in order to complete the projection, namely, to fix the position of the zonal arc  $[bsos'b]$ , by determining the position of one of the poles on it, for the other poles will then also be fixed by the intersections of this arc with the arcs just drawn. The pole  $s'$  was taken for the purpose, the pole P' of the zone  $[at's'a]$  being first found in a similar manner to P, the angle  $as'$  marked off from  $a=(\bar{1}00)$  along the left half of the primitive circle and the point marked off joined to P', cutting the zonal arc at the facial pole  $s'$  required. We then have three points  $b=(0\bar{1}0)$ ,  $s'=(\bar{1}21)$ , and  $b=(010)$  on the zonal arc and can construct it, the poles

$o=(\bar{1}11)$ , and  $s=(\bar{1}21)$  being determined by the intersections with the arcs from  $a$  through  $q$  and  $t$ . If our construction has been an accurate one, it will then be found that another arc drawn to pass through the two  $p$ -poles and  $t$  will also pass through  $o=(\bar{1}11)$ ; also that arcs drawn to terminate at the two  $p'$ -poles and to pass respectively through  $c=(001)$ ,  $q=(011)$ , and  $t=(021)$  will also pass through  $o=(\bar{1}11)$ ,  $s=(\bar{1}21)$ , and  $v=(\bar{1}31)$  in the several cases, and further, that the zone  $[p''qp'']$  also passes through  $v$ . The zone  $[ac]$  contains no other poles than  $a=(100)$ ,  $c=(001)$ , and  $a=(\bar{1}00)$ , but it should be drawn, being a primary zone. Having drawn all these zonal arcs and labelled the facial poles with their proper indices, the stereographic projection is completed, and what appeared at first sight to be a difficult geometrical problem is found in reality to be remarkably simple.

The  $v$ -faces  $(\bar{1}31)$  and  $(1\bar{3}\bar{1})$  are not shown on the drawing of the crystal, Fig. 227, as it was found that they would only appear as a line in each case truncating the little edges  $bs$  at the top right and lower left corners of the crystal, the line of sight being parallel to the faces; they were very small, but gave excellent reflections of the signal.

The indices of the face  $v$  are readily found by cross-multiplication of any two of the three zones at the intersection of which it lies; for instance, the zones  $[tp']$  and  $[bs]$ .

$$\begin{array}{rcccl}
 0 & 2 & 1 & 0 & 2 & 1 \\
 & \times & \times & \times & & \\
 \bar{1} & 1 & 0 & \bar{1} & 1 & 0 & [\bar{1}\bar{1}2] \\
 & & & & & & \bar{1} & \bar{1} & 2 & \bar{1} & \bar{1} & 2 \\
 & & & & & & \times & \times & \times & & & (\bar{1}31) \\
 0 & 1 & 0 & 0 & 1 & 0 & [101] \\
 & \times & \times & \times & & & 1 & 0 & 1 & 1 & 0 & 1 \\
 \bar{1} & 2 & 1 & \bar{1} & 2 & 1 & & & & & & 
 \end{array}$$

The indices of  $p''$ ,  $t$ ,  $t'$ ,  $s$ , and  $s'$  will all be found to be correct as given, when we come to the use of the anharmonic ratio of four poles in a zone involving each of them, for the calculation of the angles, assuming the indices in the first place, as these forms have been previously observed by former investigators and their descriptions obviously tallied. The indices  $\{\bar{1}31\}$  of the form  $v$  above found by cross-multiplication will be shown to be further confirmed by the calculation of the angles involving it from the anharmonic ratio, in the case of one of the zones. The prism  $\{130\}$  observed by Barker was not developed on any of the crystals obtained by the author, nor was the form  $131$  which had been observed in the year 1905 by Boeris.

The results of the measurements given in detail in the foregoing description of the practical work on this typical crystal of copper sulphate will be found tabulated at the end of the chapter, the mean value of the two individual values obtained for each angle, derived from the centrosymmetrically parallel faces, being taken as the observed angle. The calculated values are given alongside, and to these calculations we will now proceed. Although they are the most difficult that have to be tackled, right angles being entirely absent, they will all be found to be quite readily carried out with the aid of the few formulæ of Chapter VII., and the anharmonic ratio of Chapter VI.

**The Calculations—Basal Angles.**—In accordance with the explanation in Chapter VII., five basal angles are required for the calculation of the elements and the remaining angles, in the case (the general one) of a triclinic crystal. The following five were selected as having been measured with particularly good faces :

$$\begin{aligned} bp' &= (0\bar{1}0) : (1\bar{1}0) = 69^\circ 49', \\ p'p &= (1\bar{1}0) : (110) = 57^\circ 9', & \text{By difference from } 180^\circ, bp &= 53^\circ 2'. \\ bq &= (010) : (011) = 64^\circ 43', \\ bq' &= (0\bar{1}0) : (0\bar{1}1) = 58^\circ 10', & \text{,,} & \text{,,} & qq' &= 57^\circ 7'. \\ aq &= (100) : (011) = 69^\circ 43'. \end{aligned}$$

The procedure will be, to begin by employing the first two basal angles to find all the other angles in the primitive-circle zone, then to use the third and fourth to calculate the angles in the zone  $[bqc]$ ; for both zones the method will be the use of the anharmonic ratio of four poles. Having calculated all the angles in these two important zones we can employ the fifth basal angle along with two of those already determined for the calculation of the angle at  $b$  between the two zones, which is the element  $\beta$ , and with the aid of that we can further connect the two zones by the determination of the arc  $ac$ . Knowing then the three primary angles  $ab$ ,  $bc$ , and  $ac$ , as well as  $\beta$  the angle at  $b$ , we can readily calculate the two other angular elements  $\alpha$  and  $\gamma$ , which are the angles respectively at  $a$  and at  $c$ . The data then accumulated will also be found to be ample to enable us to calculate the ratio of the axes,  $a : b : c$ .

A few other calculations on similar lines will finally enable us to determine all the other angles which have been measured.

**Primitive circle zone. To find  $ab = (100) : (010)$ .**

We employ the anharmonic ratio of the four poles  $b$ ,  $p$ ,  $a$ ,  $p'$ , which we can write down directly from the data given in Fig. 229.

$$\begin{array}{l} \begin{array}{l} b \bullet 010 \\ \vdots \\ p \bullet 110 \\ \vdots \\ a \bullet 100 \\ \vdots \\ p' \bullet 1\bar{1}0 \end{array} \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \begin{array}{l} \\ 53^\circ 2' \\ \\ 57^\circ 9' \end{array} \\ \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} 110^\circ 11' \end{array}$$

$$\begin{aligned} & \begin{array}{ccccccc} & & 010 & 1\bar{1}0 & & & \\ & & \times & \times & & & \\ \frac{\sin bp}{\sin ba} \cdot \frac{\sin p'a}{\sin p'p} & = & \frac{110}{010} \cdot \frac{100}{1\bar{1}0} & & & & \\ & & \times & \times & & & \\ & & 100 & 110 & & & \\ \frac{\sin 53^\circ 2'}{\sin ba} \cdot \frac{\sin p'a}{\sin 57^\circ 9'} & = & \frac{1}{1} \cdot \frac{1}{2} = \frac{1}{2} & & & & \\ \frac{\sin p'a}{\sin ba} & = & \frac{\sin 57^\circ 9'}{2 \sin 53^\circ 2'} = \tan \theta & & & & \end{array} \\ & \text{as suggested in formula (a) on page 91, Chapter VI.} \\ & \theta = 27^\circ 44'. \end{aligned}$$

FIG. 229.

Then, from formula (e) of Chapter VI., page 92, we have :

$$\begin{aligned} \tan \frac{ba - p'a}{2} &= \tan \frac{ba + p'a}{2} \cdot \tan (45^\circ - \theta) \\ &= \tan 55^\circ 5\frac{1}{2}' \cdot \tan 17^\circ 16' \\ \frac{ba - p'a}{2} &= 24^\circ 0\frac{1}{2}'; \quad ba - p'a = 48^\circ 1'. \end{aligned}$$



We have now, therefore,

$$ba + p'a = 110^\circ 11'$$

$$ba - p'a = 48^\circ 1'.$$

By addition

$$2ab = 158^\circ 12', \text{ and } ab = 79^\circ 6'.$$

And by subtraction

$$2ap' = 62^\circ 10', \text{ and } ap' = 31^\circ 5'.$$

By difference also

$$ap = pp' - ap' = 57^\circ 9' - 31^\circ 5' = 26^\circ 4'.$$

To find  $bp'' = (0\bar{1}0) : (1\bar{2}0)$ . The four poles of which we use the anharmonic ratio are shown in Fig. 230, from which we get :

$$\begin{array}{c} 0\bar{1}0 \quad 100 \\ \times \quad \times \\ \sin bp'' \cdot \sin ap' = \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4} \\ \sin bp' \cdot \sin ap'' = \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4} \\ \times \quad \times \\ 1\bar{1}0 \quad 1\bar{2}0 \end{array}$$

$$\frac{\sin bp''}{\sin ap''} = \frac{\sin bp'}{\sin ap'} = \frac{\sin 69^\circ 49'}{2 \sin 31^\circ 5'} = \tan \theta. \quad \theta = 42^\circ 16'.$$

$$\tan \frac{ap'' - bp''}{2} = \tan \frac{ap'' + bp''}{2} \cdot \tan (45^\circ - \theta)$$

$$= \tan 50^\circ 27' \cdot \tan 2^\circ 44'.$$

$$\frac{ap'' - bp''}{2} = 3^\circ 18\frac{1}{2}'; \quad ap'' - bp'' = 6^\circ 37'.$$

We have now

$$ap'' + bp'' = 100^\circ 54'$$

$$ap'' - bp'' = 6^\circ 37'.$$

By subtraction

$$2bp'' = 94^\circ 17', \text{ and } bp'' = 47^\circ 9'.$$

Then also

$$p''p' = bp' - bp'' = 69^\circ 49' - 47^\circ 9' = 22^\circ 40'.$$

This completes the zone of the primitive circle, the prism zone.

Zone  $[bcq]$ . To find  $bt = (010) : (021)$ .

The four poles are set out in Fig. 231, and their anharmonic ratio is :

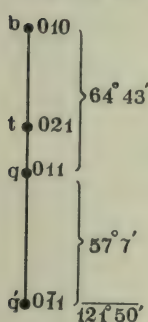


FIG. 231.

$$\begin{array}{c} 010 \quad 0\bar{1}1 \\ \times \quad \times \\ \sin bt \cdot \sin q'q = \frac{0}{2} \cdot \frac{1}{1} = \frac{0}{2} \\ \sin bq \cdot \sin q't = \frac{0}{1} \cdot \frac{1}{1} = \frac{0}{1} \\ \times \quad \times \\ 011 \quad 021 \end{array}$$

$$\frac{\sin bt}{\sin q't} = \frac{2 \sin 64^\circ 43'}{3 \sin 57^\circ 7'} = \tan \theta. \quad \theta = 35^\circ 40'.$$

$$\tan \frac{q't - bt}{2} = \tan \frac{q't + bt}{2} \cdot \tan (45^\circ - \theta).$$

$$= \tan 60^\circ 55' \tan 9^\circ 20'.$$

$$\frac{q't - bt}{2} = 16^\circ 28', \quad q't - bt = 32^\circ 56'.$$

We now know that :

$$q't + bt = 121^\circ 50',$$

$$q't - bt = 32^\circ 56'.$$

By subtraction

$$2bt = 88^\circ 54', \text{ and } bt = 44^\circ 27'.$$

Then also :

$$tq = bq - bt = 64^\circ 43' - 44^\circ 27' = 20^\circ 16'.$$

To find  $bc = (010) : (001)$ .

The four poles the anharmonic ratio of which we use are diagrammatically set out in Fig. 232. The ratio is as follows :

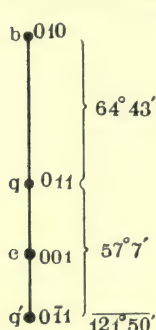


FIG. 232.

By addition  
and by subtraction  
Moreover,

$$\begin{aligned} \frac{\sin 64^\circ 43'}{\sin bc} \cdot \frac{\sin q'c}{\sin 57^\circ 7'} &= \frac{011}{010} \cdot \frac{001}{011\bar{1}} = \frac{1}{1} \cdot \frac{\bar{1}}{2} = \frac{1}{2}, \\ \frac{\sin q'c}{\sin bc} &= \frac{\sin 57^\circ 7'}{2 \sin 64^\circ 43'} = \tan \theta, \quad \theta = 24^\circ 54\frac{1}{2}', \\ \tan \frac{bc - q'c}{2} &= \tan \frac{bc + q'c}{2} \cdot \tan (45^\circ - \theta), \\ &= \tan 60^\circ 55' \tan 20^\circ 5\frac{1}{2}', \\ \frac{1}{2}(bc - q'c) &= 33^\circ 20', \text{ and } bc - q'c = 66^\circ 40'. \end{aligned}$$

The following are now, therefore, known:

$$\begin{aligned} bc + q'c &= 121^\circ 50' \\ bc - q'c &= 66^\circ 40'. \end{aligned}$$

$$\begin{aligned} 2bc &= 188^\circ 30', \text{ and } bc = 94^\circ 15', \\ 2q'c &= 55^\circ 10', \text{ and } q'c = 27^\circ 35'. \end{aligned}$$

$$cq = qq' - cq' = 57^\circ 7' - 27^\circ 35' = 29^\circ 32'.$$

To find  $bt' = (0\bar{1}0) : (0\bar{2}1)$ .

The anharmonic ratio to be used will be clear from Fig. 233.

$$\begin{aligned} \frac{\sin bt'}{\sin 58^\circ 10'} \cdot \frac{\sin 27^\circ 35'}{\sin ct'} &= \frac{0\bar{1}0}{0\bar{2}1} \cdot \frac{001}{001\bar{1}} = \frac{\bar{1}}{1} \cdot \frac{1}{2} = \frac{1}{2} \\ \frac{\sin bt'}{\sin ct'} &= \frac{\sin 58^\circ 10'}{2 \sin 27^\circ 35'} = \tan \theta, \quad \theta = 42^\circ 32'. \\ \tan \frac{ct' - bt'}{2} &= \tan \frac{ct' + bt'}{2} \cdot \tan (45^\circ - \theta) = \tan 42^\circ 52\frac{1}{2}' \cdot \tan 2^\circ 28'. \\ \frac{1}{2}(ct' - bt') &= 2^\circ 17\frac{1}{2}'. \end{aligned}$$

The known data are now:

$$\begin{aligned} ct' + bt' &= 85^\circ 45' \\ ct' - bt' &= 4^\circ 35'. \end{aligned}$$

Subtracting:

$$2bt' = 81^\circ 10', \text{ and } bt' = 40^\circ 35'.$$

Also:

$$t'q' = bq' - bt' = 58^\circ 10' - 40^\circ 35' = 17^\circ 35'.$$

This completes the calculation of the second important zone  $[bqc]$ .

To find the angle at  $b$  between these two zones, that is,  $\beta$ , knowing the three sides of the triangle  $aqb$  containing it.

We employ formula (a) on page 109, Chapter VII. The three sides are:

$$\begin{aligned} aq &= 69^\circ 43' \\ bq &= 64^\circ 43' \\ ab &= 79^\circ 6' \end{aligned}$$

$$\begin{aligned} \text{sum} &= 213^\circ 32' \text{ and } s = \frac{1}{2} \text{ sum} = 106^\circ 46' \\ &\quad 42^\circ 3' \qquad \qquad \qquad 27^\circ 40' \end{aligned}$$

$$\sin^2 \frac{\beta}{2} = \frac{\sin (106^\circ 46' - 64^\circ 43') \cdot \sin (106^\circ 46' - 79^\circ 6')}{\sin 64^\circ 43' \cdot \sin 79^\circ 6'}$$

$$\frac{\beta}{2} = 36^\circ 17', \text{ and } \beta = 72^\circ 34'.$$

The upper front angle between the axes  $a$  and  $c$  is the supplementary axial angle  $\beta = 107^\circ 26'$ .

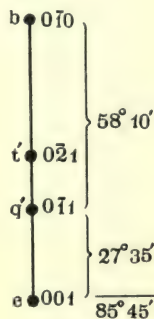


FIG. 233.

**To find  $ac$**   $= (100) : (001)$  in the triangle  $abc$ , knowing the two sides  $bc = 94^\circ 15'$  and  $ab = 79^\circ 6'$ , and the included angle at  $b = 72^\circ 34'$ , by the formulæ (b) of page 109, Chapter VII.

$$\tan \theta = \tan 79^\circ 6' \cdot \cos 72^\circ 34'; \quad \cos ac = \frac{\cos 79^\circ 6' \cdot \cos (94^\circ 15' - \theta')}{\cos \theta}$$

$$\theta = 57^\circ 16'. \quad ac = 73^\circ 47'.$$

We are now in a position to be able to calculate the other two axial angles  $\alpha$  and  $\gamma$ , for we know all three sides of the primary triangle  $abc$ , namely,  $ab = 79^\circ 6'$ ,  $bc = 94^\circ 15'$ , and  $ac = 73^\circ 47'$ .

**To find  $\alpha$ .**

By formula (a) of Chapter VII.:

$$\sin^2 \frac{\alpha}{2} = \frac{\sin (123^\circ 34' - 73^\circ 47') \cdot \sin (123^\circ 34' - 79^\circ 6')}{\sin 73^\circ 47' \cdot \sin 79^\circ 6'}$$

$$\frac{\alpha}{2} = 48^\circ 52', \text{ and } \alpha = 97^\circ 44'.$$

The upper right-hand angle between the axes  $b$  and  $c$  is the supplementary axial angle  $\alpha = 82^\circ 16'$ .

**To find  $\gamma$ .**

$$\sin^2 \frac{\gamma}{2} = \frac{\sin (123^\circ 34' - 94^\circ 15') \cdot \sin (123^\circ 34' - 73^\circ 47')}{\sin 94^\circ 15' \cdot \sin 73^\circ 47'}$$

$$\text{or } \cos 4^\circ 15'.$$

$$\frac{\gamma}{2} = 38^\circ 40', \text{ and } \gamma = 77^\circ 20'.$$

The front right-hand angle between the axes  $a$  and  $b$  is the supplementary axial angle  $\gamma = 102^\circ 40'$ .

We have thus completed the calculation of the three axial angles  $\alpha$ ,  $\beta$ , and  $\gamma$ .

**To find the axial ratio** we require to find first the four angles,  $\chi$ ,  $\psi$ ,  $\theta$ , and  $\phi$  in accordance with Chapter VII. They are shown in Fig. 54, page 111.

We can at once find  $\chi$  and  $\psi$  knowing, as we do, the three sides of each of the triangles  $abq$  and  $acq$ .

In the triangle  $abq$  half the sum of the sides has already been shown to be  $106^\circ 46'$ , and the three sides are  $aq = 69^\circ 43'$ ,  $bq = 64^\circ 43'$ ,  $ab = 79^\circ 6'$ .

$$\sin^2 \frac{\chi}{2} = \frac{\sin (106^\circ 46' - 69^\circ 43') \cdot \sin (106^\circ 46' - 79^\circ 6')}{\sin 69^\circ 43' \cdot \sin 79^\circ 6'}$$

$$\frac{\chi}{2} = 33^\circ 27', \text{ and } \chi = 66^\circ 54'.$$

In the triangle  $acq$  the three sides are  $ac = 73^\circ 47'$ ,  $cq = 29^\circ 32'$ , and  $aq = 69^\circ 43'$ . The sum of these is  $173^\circ 2'$  and half the sum  $= 86^\circ 31'$ .

$$\sin^2 \frac{\psi}{2} = \frac{\sin (86^\circ 31' - 69^\circ 43') \cdot \sin (86^\circ 31' - 73^\circ 47')}{\sin 69^\circ 43' \cdot \sin 73^\circ 47'}$$

$$\frac{\psi}{2} = 15^\circ 25\frac{1}{2}', \text{ and } \psi = 30^\circ 51'.$$

$$\text{Then by page 111, Chapter VII. : } \frac{c}{b} = \frac{\sin \psi}{\sin \chi} = \frac{\sin 30^\circ 51'}{\sin 66^\circ 54'}. \quad c/b = 0.5575.$$

Before we can calculate  $\theta$  and  $\phi$ , and so  $a/b$  (which  $= \frac{\sin \theta}{\sin \phi}$ ), we must find  $cp = (001) : (110)$  from the triangle  $bcp$ , knowing the two sides  $bc = 94^\circ 15'$  and  $bp = 53^\circ 2'$ , and also the included angle  $\beta = 72^\circ 34'$ .



By formula (b) page 109, Chapter VII. :

$$\tan \theta = \tan 53^\circ 2' \cdot \cos 72^\circ 34'; \quad \cos cp = \frac{\cos 53^\circ 2' \cdot \cos (94^\circ 15' - \theta)}{\cos \theta}$$

$$\theta = 21^\circ 42'.$$

$$cp = 78^\circ 48'.$$

Now to find  $\theta$  and  $\phi$  knowing the three sides of each of the triangles  $acp$  and  $bcp$ .

<i>acp.</i>	<i>bcp.</i>
$ac = 73^\circ 47'$	$bc = 94^\circ 15'$
$cp = 78 \quad 48$	$cp = 78 \quad 48$
$ap = 26 \quad 4$	$bp = 53 \quad 2$
sum = 178 39	sum = 226 5
$\frac{1}{2}$ sum = 89 20	$\frac{1}{2}$ sum = 113 3
$15^\circ 33'$	$10^\circ 32'$
$\sin^2 \frac{\theta}{2} = \frac{\sin (89^\circ 20' - 73^\circ 47') \cdot \sin (89^\circ 20' - 78^\circ 48')}{\sin 73^\circ 47' \cdot \sin 78^\circ 48'}$	
$\frac{\theta}{2} = 13^\circ 11', \text{ and } \theta = 26^\circ 22'.$	
$18^\circ 48'$	$34^\circ 15'$
$\sin^2 \frac{\phi}{2} = \frac{\sin (113^\circ 3' - 94^\circ 15') \cdot \sin (113^\circ 3' - 78^\circ 48')}{\sin 94^\circ 15' \cdot \sin 78^\circ 48'}$	
or $\cos 4^\circ 15'$	
$\frac{\phi}{2} = 25^\circ 30', \text{ and } \phi = 51^\circ 0'.$	

Then from page 111, Chapter VII., we have :  $\frac{a}{b} = \frac{\sin \theta}{\sin \phi} = \frac{\sin 26^\circ 22'}{\sin 51^\circ 0'}$

$$a/b = 0.5715.$$

Hence the ratio of the axes is :  $a : b : c = 0.5715 : 1 : 0.5575$ .

Having now calculated all the elements of the crystal, as well as all the angles in the three primary zones  $[ab]$ ,  $[bc]$ , and  $[ac]$ , we have only to calculate the angles in the other zones in order to complete the work on the crystal. We shall take the various angles now in the order of convenience of calculation, not necessarily a complete zone at a time.

**To find  $pt = (110) : (021)$** , from the triangle  $bpt$ , knowing the two sides  $bt = 44^\circ 27'$  and  $bp = 53^\circ 2'$ , and the included angle  $\beta = 72^\circ 34'$ .

$$\tan \theta = \tan 44^\circ 27' \cdot \cos 72^\circ 34'; \quad \cos pt = \frac{\cos 44^\circ 27' \cdot \cos (53^\circ 2' - \theta)}{\cos \theta}$$

$$\theta = 16^\circ 23'.$$

$$pt = 53^\circ 21'.$$

**To find  $at = (100) : (021)$** , from the triangle  $abt$ , knowing the two sides  $ab = 79^\circ 6'$ , and  $bt = 44^\circ 27'$ , and the included angle  $\beta = 72^\circ 34'$ .

$$\tan \theta = \tan 44^\circ 27' \cdot \cos 72^\circ 34'; \quad \cos at = \frac{\cos 44^\circ 27' \cdot \cos (79^\circ 6' - \theta)}{\cos \theta}$$

$$\theta = 16^\circ 23' \text{ as above calculated. } at = 70^\circ 4'.$$

**To find  $at' = (100) : (0\bar{2}1)$** , from the triangle  $b = (0\bar{1}0) : t' = (0\bar{2}1) : a = (100)$ , knowing the two sides  $bt' = 40^\circ 35'$  and  $ab = 100^\circ 54'$ , and the included angle  $\beta = 72^\circ 34'$  [the angle at  $b = (0\bar{1}0)$ , which is of course equal to that at  $b = (010)$ ].

$$\tan \theta = \tan 40^\circ 35' \cdot \cos 72^\circ 34'; \quad \cos at' = \frac{\cos 40^\circ 35' \cdot \cos (100^\circ 54' - \theta)}{\cos \theta}$$

$$\theta = 14^\circ 24'.$$

$$at' = 87^\circ 15'.$$

**To find  $p'q = (1\bar{1}0) : (011)$** , from the triangle  $b = (0\bar{1}0) : q = (011) : p' = (1\bar{1}0)$ , knowing  $bq = 115^\circ 17'$ ,  $bp' = 69^\circ 49'$ , and  $\beta = 72^\circ 34'$ .

$$\tan \theta = \tan 69^\circ 49' \cdot \cos 72^\circ 34'; \quad \cos p'q = \frac{\cos 69^\circ 49' \cdot \cos (115^\circ 17' - \theta)}{\cos \theta}$$

$$\theta = 39^\circ 11'. \quad p'q = 83^\circ 52'.$$

We now come to the more difficult part of this calculation. So far, we have been able to proceed straightforwardly, triangles with three known elements, or anharmonic ratios, lying clearly before us. It will be found that the next step may most conveniently be the calculation of the two sides  $qs$  and  $st$  in the triangle  $q = (011) : s = (\bar{1}21) : t = (021)$ , although we at present only know one element, the side  $qt = 20^\circ 16'$ . But the angle at  $q$  is equal to the angle at  $q$  in the last triangle considered,  $bqp'$ , and the angle at  $t$  is similarly the same as that at  $t$  in the triangle  $b = (010) : t = (021) : a = (100)$ . Now these angles at  $q$  and  $t$  can be readily calculated from the two triangles referred to, in which more than an adequate number of elements are known, so we proceed first to these two calculations.

To find the angle at  $q = (011)$  in the triangle  $b = (0\bar{1}0) : q = (011) : p' = (011)$ , from the three following elements summed in the left column, and to find the angle at  $t = (021)$  in the triangle  $abt$  from the three known elements summed in the right column below.

$bq = 115^\circ 17'$	$ab = 79^\circ 6'$
$bp' = 69 49$	$bt = 44 27$
$qp' = 83 52$	$at = 70 4$
<hr/>	<hr/>
sum = 268 58	sum = 193 37
$\frac{1}{2}$ sum = 134 29	$\frac{1}{2}$ sum = 96 49
$19^\circ 12'$	$50^\circ 37'$
$\sin^2 \frac{q}{2} = \frac{\sin (134^\circ 29' - 115^\circ 17') \cdot \sin (134^\circ 29' - 83^\circ 52')}{\sin 115^\circ 17' \cdot \sin 83^\circ 52'}$	
$\text{or } \cos 25^\circ 17'$	
$\frac{q}{2} = 32^\circ 7', \text{ and } q = 64^\circ 14'.$	
$52^\circ 22'$	$26^\circ 45'$
$\sin^2 \frac{t}{2} = \frac{\sin (96^\circ 49' - 44^\circ 27') \cdot \sin (96^\circ 49' - 70^\circ 4')}{\sin 44^\circ 27' \cdot \sin 70^\circ 4'}$	
$\frac{t}{2} = 47^\circ 23', \text{ and } t = 94^\circ 46'.$	

To find now  $qs = (011) : (\bar{1}21)$  and  $st = (\bar{1}21) : (021)$ , knowing the side  $qt = 20^\circ 16'$  and the two angles adjacent to it  $q = 64^\circ 14'$  and  $t = 94^\circ 46'$ .

We here for the first time employ the formula (c) of page 109, Chapter VII.

$$\tan \frac{1}{2}(qs + st) = \frac{\cos \frac{1}{2}(94^\circ 46' - 64^\circ 14')}{\cos \frac{1}{2}(94^\circ 46' + 64^\circ 14')} \cdot \tan 10^\circ 8'$$

$$\tan \frac{1}{2}(qs - st) = \frac{\sin 15^\circ 16'}{\sin 79^\circ 30'} \cdot \tan 10^\circ 8'.$$

$$\frac{1}{2}(qs + st) = 43^\circ 25'; \quad \frac{1}{2}(qs - st) = 2^\circ 44\frac{1}{2}'.$$

$$qs + st = 86^\circ 50'$$

$$qs - st = 5^\circ 29'.$$

By addition  $2qs = 92^\circ 19', \text{ and } qs = 46^\circ 9'.$

By subtraction  $2st = 81^\circ 21', \text{ and } st = 40^\circ 40'.$

Then further :  $sp' = 180^\circ - (p'q + qs) = 180^\circ - (83^\circ 52' + 46^\circ 9') = 49^\circ 59'.$   
 Also :  $as = 180^\circ - (at + ts) = 180^\circ - (70^\circ 4' + 40^\circ 40') = 69^\circ 16'.$

To find  $bs = (010) : (\bar{1}21)$ , from the triangle  $sp'b$ , knowing the two sides  $sp' = 49^\circ 59'$ , and  $bp' = 69^\circ 49'$ , and first finding the included angle at  $p'$  from the triangle  $aqp'$  in which all three sides are known as follows :

$$\begin{array}{r} ap' = 31^\circ 5' \\ p'q = 83 \ 52 \\ aq = 69 \ 43 \\ \hline \text{sum} = 184 \ 40 \quad \frac{1}{2} \text{ sum} = 92^\circ 20'. \\ \quad \quad \quad 8^\circ 28' \quad \quad \quad 61^\circ 15' \\ \sin^2 \frac{p'}{2} = \frac{\sin(92^\circ 20' - 83^\circ 52') \cdot \sin(92^\circ 20' - 31^\circ 5')}{\sin 83^\circ 52' \cdot \sin 31^\circ 5'} \\ \frac{p'}{2} = 30^\circ 6', \text{ and } p' = 60^\circ 12'. \end{array}$$

$$\begin{array}{l} \text{Then : } \tan \theta = \tan 49^\circ 59' \cdot \cos 60^\circ 12'; \cos bs = \frac{\cos 49^\circ 59' \cdot \cos(69^\circ 49' - \theta)}{\cos \theta} \\ \theta = 30^\circ 37'. \quad \quad \quad bs = 54^\circ 37'. \end{array}$$

To find  $bs'$  and  $as'$  should be our next task, from the triangle  $a = (\bar{1}00) : b = (0\bar{1}0) : s' = (\bar{1}\bar{2}1)$ , but at present we only know one element in it, the side  $ab = 79^\circ 6'$ . But we can find the adjacent angles at  $a$  and  $b$ , the former from the triangle  $abt'$  and the latter from the triangle  $bsp'$ , knowing the three sides in each case. We shall proceed, therefore, first to find these two angles, the three sides being summed as under in the two cases :

Triangle $abt'$ .	Triangle $bsp'$ .
$ab = 100^\circ 54'$	$bs = 54^\circ 37'$
$at' = 87 \ 15$	$sp' = 49 \ 59$
$bt' = 40 \ 35$	$bp' = 69 \ 49$
<hr style="width: 100%;"/>	<hr style="width: 100%;"/>
$\text{sum} = 228 \ 44$	$\text{sum} = 174 \ 25$
$\frac{1}{2} \text{ sum} = 114 \ 22$	$\frac{1}{2} \text{ sum} = 87 \ 13$
$\quad \quad \quad 13^\circ 28'$	$\quad \quad \quad 27^\circ 7'$
$\sin^2 \frac{a}{2} = \frac{\sin(114^\circ 22' - 100^\circ 54') \cdot \sin(114^\circ 22' - 87^\circ 15')}{\sin 100^\circ 54' \cdot \sin 87^\circ 15'}.$	$\sin^2 \frac{b}{2} = \frac{\sin(87^\circ 13' - 54^\circ 37') \cdot \sin(87^\circ 13' - 69^\circ 49')}{\sin 54^\circ 37' \cdot \sin 69^\circ 49'}.$
$\frac{a}{2} = 19^\circ 12', \text{ and } a = 38^\circ 24'.$	$\frac{b}{2} = 27^\circ 19', \text{ and } b = 54^\circ 38'.$

We are now in a position to proceed with the calculation of  $bs' = (0\bar{1}0) : (\bar{1}\bar{2}1)$  and  $as' = (\bar{1}00) : (\bar{1}\bar{2}1)$  from the triangle  $a = (\bar{1}00) : b = (0\bar{1}0) : s' = (\bar{1}\bar{2}1)$ , knowing the side  $ab = 79^\circ 6'$  and the two adjacent angles  $a = 38^\circ 24'$  and  $b = 54^\circ 38'$ , employing the formula (c) of page 109, Chapter VII.

$$\begin{array}{l} \tan \frac{1}{2}(as' + bs') = \frac{\cos \frac{1}{2}(54^\circ 38' - 38^\circ 24')}{\cos \frac{1}{2}(54^\circ 38' + 38^\circ 24')} \cdot \tan 39^\circ 33' \\ \quad \quad \quad 93^\circ 2' \\ \tan \frac{1}{2}(as' - bs') = \frac{\sin 8^\circ 7'}{\sin 46^\circ 31'} \cdot \tan 39^\circ 33'. \end{array}$$



$$\begin{aligned}
 \frac{1}{2}(as' + bs') &= 49^\circ 55'. & \frac{1}{2}(as - bs') &= 9^\circ 8'. \\
 \text{Hence,} & as' + bs' &= 99^\circ 50' \\
 \text{and} & as' - bs' &= 18^\circ 16'. \\
 \text{Adding,} & 2as' &= 118^\circ 6', \text{ and } as' = 59^\circ 3'. \\
 \text{Subtracting,} & 2bs' &= 81^\circ 34', \text{ and } bs' = 40^\circ 47'. \\
 \text{Then:} & s't' = 180^\circ - (as' + at') &= 180^\circ - (59^\circ 3' + 87^\circ 15') = 33^\circ 42'. \\
 \text{Also:} & s's = 180^\circ - (bs' + bs) &= 180^\circ - (40^\circ 47' + 54^\circ 37') = 84^\circ 36'.
 \end{aligned}$$

We are now in a position to complete the calculation of the angles in the zone [bso] by finding *so* and *s'o*, and thus determining the position of the primary pyramid  $o = (\bar{1}11)$ , employing our knowledge of *bs'* and *s's* in the anharmonic ratio of the four poles  $b = (0\bar{1}0)$ ,  $s' = (\bar{1}\bar{2}1)$ ,  $o = (\bar{1}11)$ , and  $s = (\bar{1}21)$ . The conditions are shown in Fig. 234, and the ratio runs as under:

$$\begin{array}{c}
 0\bar{1}0 \quad \bar{1}\bar{2}1 \\
 \times \quad \times \\
 \sin bs' \cdot \sin so = \frac{\bar{1}\bar{2}1}{0\bar{1}0} \cdot \frac{\bar{1}11}{\bar{1}\bar{2}1} = \frac{\bar{1}}{1} \cdot \frac{1}{4} \\
 \times \quad \times \\
 \bar{1}11 \quad \bar{1}\bar{2}1
 \end{array}$$

$$\frac{\sin so}{\sin bo} = \frac{\sin 84^\circ 36'}{4 \sin 40^\circ 47'} = \tan \theta.$$

$$\theta = 20^\circ 51\frac{1}{2}'.$$

$$\begin{aligned}
 \text{Then:} \quad \tan \frac{1}{2}(bo - so) &= \tan \frac{1}{2}(bo + so) \cdot \tan 45^\circ - \theta' \\
 &= \tan 62^\circ 41\frac{1}{2}' \cdot \tan 24^\circ 8\frac{1}{2}'.
 \end{aligned}$$

$$\frac{1}{2}(bo - so) = 40^\circ 57\frac{1}{2}'.$$

$$bo + so = 125^\circ 23'.$$

$$bo - so = 81^\circ 55'.$$

We then have  
and

$$2bo = 207^\circ 18' \text{ and } bo = 103^\circ 39';$$

$$2so = 43^\circ 28' \text{ and } so = 21^\circ 44'.$$

$$\text{Then } s'o = bo - bs' = 103^\circ 39' - 40^\circ 47' = 62^\circ 52'.$$

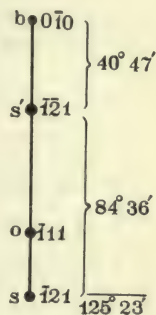


FIG. 234.

To find  $bv = (010) : (\bar{1}31)$  and  $vs = (\bar{1}31) : (\bar{1}21)$ . The indices of the form *v* have been shown to be  $\{\bar{1}31\}$ , from its position at the intersection of the zones [bso] and [*p't*]. We can find the position of either of the two parallel *v*-faces in the zone [bso] from the anharmonic ratio, the conditions for which are set forth in Fig. 235. The ratio is as under:

$$\begin{array}{c}
 010 \quad \bar{1}11 \\
 \times \quad \times \\
 \sin bv \cdot \sin os = \frac{\bar{1}31}{010} \cdot \frac{\bar{1}\bar{2}1}{\bar{1}11} = \frac{1}{1} \cdot \frac{\bar{1}}{2} = \frac{1}{2}, \\
 \times \quad \times \\
 \bar{1}21 \quad \bar{1}31
 \end{array}$$

$$\frac{\sin bv}{\sin ov} = \frac{\sin 54^\circ 37'}{2 \sin 21^\circ 44'} = \tan \theta'. \quad \theta = 47^\circ 45'.$$

$$\begin{aligned}
 \tan \frac{1}{2}(ov - bv) &= \tan \frac{1}{2}(ov + bv) \cdot \tan (45^\circ - \theta) \\
 &= \tan 38^\circ 10\frac{1}{2}' \cdot \tan (-2^\circ 45') \\
 &= -(\tan 38^\circ 10\frac{1}{2}' \cdot \tan 2^\circ 45')
 \end{aligned}$$

$$\frac{1}{2}(ov - bv) = -2^\circ 10',$$

$$ov - bv = -4^\circ 20',$$

$$bv - ov = 4^\circ 20'.$$

$$bv + ov = 76^\circ 21'.$$

and  
or

We also have

$$2bv = 80^\circ 41', \text{ and } bv = 40^\circ 21'.$$

$$2ov = 72^\circ 1', \text{ and } ov = 36^\circ 0'.$$

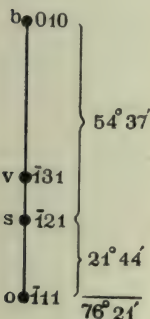


FIG. 235.

Adding,

Subtracting,

Then also :

$$vs = ov - os = 36^\circ 0' - 21^\circ 44' = 14^\circ 16'.$$

This completes the important zone [*bso*].

**To find**  $ao = (\bar{1}00) : (\bar{1}11)$ , knowing two sides and the included angle of the triangle  $a = (\bar{1}00) : b = (010) : o = (\bar{1}11)$ , namely,  $ab = 100^\circ 54'$ ,  $bo = 76^\circ 21'$ , and the angle at  $b = 54^\circ 38'$ . The angle  $bo$  is the supplement of the angle  $bo$  just found.

$$\tan \theta = \tan 76^\circ 21' \cdot \cos 54^\circ 38'; \quad \cos ao = \frac{\cos 76^\circ 21' \cdot \cos (100^\circ 54' - \theta)}{\cos \theta}.$$

$$\theta = 67^\circ 14'. \quad ao = 59^\circ 30'.$$

Then :

$$oq = 180^\circ - (ao + aq) = 180^\circ - (59^\circ 30' + 69^\circ 43') = 50^\circ 47'.$$

There is one more measured angle to calculate, namely,  $po = (\bar{1}\bar{1}0) : (\bar{1}11)$ , from the triangle  $p = (\bar{1}\bar{1}0) : o = (\bar{1}11) : b = (010)$ , of which we know the two sides  $pb = 53^\circ 2'$  and  $bo = 103^\circ 39'$ , and the included angle at  $b = 54^\circ 38'$ .

$$\tan \theta = \tan 53^\circ 2' \cdot \cos 54^\circ 38'; \quad \cos po = \frac{\cos 53^\circ 2' \cdot \cos (103^\circ 39' - \theta)}{\cos \theta}$$

$$\theta = 37^\circ 34'. \quad po = 72^\circ 5'.$$

$$\text{Then also } ot = 180^\circ - (po + pt) = 180^\circ - (72^\circ 5' + 53^\circ 21') = 54^\circ 34'.$$

This finally completes the calculations for copper sulphate.

They have been longer than in the cases of the typical crystals of the systems of higher symmetry, and their relative difficulty has been about as great as will ever be met with, except perhaps in the cases of crystals exceptionally rich in faces belonging to forms of higher indices. Yet they have all proved perfectly straightforward, and the few formulæ given in Chapter VII. and the anharmonic ratio of Chapter VI. have sufficed to carry them out completely. This should prove a source of satisfaction to all who endeavour to follow the lines of progress in crystallography laid down in this book, for it demonstrates that if the few principles and the small amount of simple mathematics indicated in those two chapters have been mastered, all difficulties will have passed away. Even in the cases of the investigations of such exceptionally rich crystals as have just been alluded to, any additional formulæ will only be required for the calculation of one or two angles, and will be one or other of the formulæ of spherical trigonometry not included in Chapter VII., but which are given in every elementary text-book on that subject.

The mean angular values derived from the whole twelve crystals measured were so nearly identical with those derived from the typical crystal alone, that only the latter are included in the final table of angles and elements which will now be given. For instance, 12 independent irreproachable values of the angle  $bt = (010) : (021)$  were obtained, all within the limits  $44^\circ 24'$  to  $44^\circ 32'$ , and the mean was  $44^\circ 28'$ , identical with the mean value of the two measurements on the typical crystal. We can thus rely with full confidence on the observed values derived from the best individual crystal, which in this case is the example chosen to represent typical triclinic symmetry.

SUMMARY OF RESULTS FOR CRYSTAL OF COPPER SULPHATE  
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

**Crystal-system :** Triclinic. **Class :** pinakoidal-holohedral.

**Habit :** prismatic.

**Axial Angles :**  $\alpha = 82^\circ 16'$ ,  $\beta = 107^\circ 26'$ ,  $\gamma = 102^\circ 40'$ .

**Ratio of Axes :**  $a : b : c = 0.5715 : 1 : 0.5575$ .

**Forms observed :**  $a = \{100\}$ ,  $b = \{010\}$ ,  $c = \{001\}$ ,  $p = \{110\}$ ,  $p' = \{1\bar{1}0\}$ ,  
 $p'' = \{1\bar{2}0\}$ ,  $q = \{011\}$ ,  $q' = \{0\bar{1}1\}$ ,  $t = \{021\}$ ,  $t' = \{0\bar{2}1\}$ ,  $o = \{111\}$ ,  $s = \{121\}$ ,  
 $s' = \{1\bar{2}1\}$ ,  $v = \{131\}$ .

Each of these forms consists of a pair of parallel faces, or pinakoid, only, in accordance with holohedral triclinic symmetry.

The prism zone was always the most prominently developed, on the crystals of the numerous crops examined by the author, and usually the two primary prismatic pinakoids  $p = \{110\}$  and  $p' = \{1\bar{1}0\}$  were represented by the largest faces in it, although the brachy-pinakoid faces  $b = \{010\}$  and  $b' = \{0\bar{1}0\}$  were occasionally quite as broad. The two faces of the macro-pinakoid  $a = \{100\}$  were generally narrower. The faces of the secondary prismatic pinakoid  $p'' = \{1\bar{2}0\}$  were generally well-developed, although sometimes narrow. The prismatic pinakoid  $\{1\bar{3}0\}$  observed by Barker was never met with on the dozen crystals measured, of which the typical crystal here described was the most perfect. Of the end-forms the two parallel faces of the primary pyramidal pinakoid  $o = \{111\}$  were usually predominating, but the crystals of certain crops showed instead a more prominent development of the two forms  $t = \{021\}$  and  $s = \{121\}$ , or  $t$  and  $s' = \{1\bar{2}1\}$ . The basal pinakoid  $c = \{001\}$  was very small, and in fact was only found with measurable faces on one crystal, the typical one chosen as example.

The elements found by Barker, as given by von Groth on page 349 of the fourth edition of his *Physikalische Krystallographie*, and also on page 419 of his *Chemische Krystallographie*, Part II., 1908, the details being unpublished, are :  $\alpha = 82^\circ 5'$ ,  $\beta = 107^\circ 8'$ ,  $\gamma = 102^\circ 41'$ ; and  $a : b : c = 0.5721 : 1 : 0.5554$ . If we assume that Kupffer's values for  $\alpha$  and  $\gamma$  are the supplements of the real axial angles, while his value for  $\beta$  is the real value, then his corrected real values would stand as follows :  $\alpha = 82^\circ 21'$ ,  $\beta = 106^\circ 49'$ ,  $\gamma = 102^\circ 23'$ . The values of all three observers are then not far removed from each other, considering the difficulty of obtaining absolutely perfect crystals, and the general agreement between the values now given by the author and those of Barker is fairly satisfactory, and shows that no error has been made in regard to the recognition of the various faces in the two descriptions.

The interfacial angles are given in the accompanying table, in which the mean observed values derived from the typical perfect crystal are set down alongside the calculated values. The agreement of the two columns affords the final proof of the trustworthiness of the results.



## CRYSTAL ANGLES OF COPPER SULPHATE.

Angle.	No. of Measurements.	Limits.	Observed.	Calculated.	Difference.
$ab = 100 : 010$	2	79° 1' - 79° 7'	79° 4'	79° 6'	2'
$bp = 010 : 110$	2	53 0 - 53 4	53 2	53 2	0
$pa = 110 : 100$	2	26 1 - 26 3	26 2	26 4	2
$ap' = 100 : \bar{1}\bar{1}0$	2	31 6 - 31 8	31 7	31 5	2
$pp' = 110 : \bar{1}\bar{1}0$	2	57 9 - 57 9	57 9	*	..
$p'p'' = \bar{1}\bar{1}0 : 120$	2	22 32 - 22 36	22 34	22 40	6
$p''b = 120 : 0\bar{1}0$	2	47 10 - 47 20	47 15	47 9	6
$p'b = \bar{1}\bar{1}0 : 0\bar{1}0$	2	69 46 - 69 52	69 49	*	..
$bc = 010 : 001$	2	94 17 - 94 23	94 20	94 15	5
$bt = 010 : 021$	2	44 25 - 44 30	44 28	44 27	1
$tq = 021 : 011$	2	20 14 - 20 16	20 15	20 16	1
$bq = 010 : 011$	2	64 39 - 64 46	64 43	*	..
$qc = 011 : 001$	2	29 37 - 29 38	29 37	29 32	5
$cq' = 001 : 0\bar{1}\bar{1}$	2	27 30 - 27 31	27 31	27 35	4
$qq' = 011 : 0\bar{1}\bar{1}$	2	57 7 - 57 9	57 8	57 7	1
$q't' = 0\bar{1}\bar{1} : 021$	2	17 25 - 17 33	17 29	17 35	6
$t'b = 021 : 0\bar{1}0$	2	40 34 - 40 47	40 41	40 35	6
$q'b = 0\bar{1}\bar{1} : 0\bar{1}0$	2	58 7 - 58 12	58 10	*	..
$ac = 100 : 001$	..	..	..	73 47	..
$aq = 100 : 011$	2	69 43 - 69 43	69 43	*	..
$qo = 011 : \bar{1}\bar{1}1$	2	50 40 - 50 42	50 41	50 47	6
$oa = \bar{1}\bar{1}1 : \bar{1}00$	2	59 35 - 59 37	59 36	59 30	6
$at = 100 : 021$	2	70 6 - 70 9	70 7	70 4	3
$ts = 021 : \bar{1}21$	2	40 36 - 40 38	40 37	40 40	3
$sa = \bar{1}21 : \bar{1}00$	2	69 13 - 69 18	69 16	69 16	0
$at' = 100 : 0\bar{2}\bar{1}$	2	87 11 - 87 15	87 13	87 15	2
$t's' = 0\bar{2}\bar{1} : \bar{1}21$	2	33 41 - 33 46	33 43	33 42	1
$s'a = \bar{1}21 : \bar{1}00$	2	58 59 - 59 8	59 4	59 3	1
$bv = 010 : \bar{1}31$	2	40 22 - 40 22	40 22	40 21	1
$vs = \bar{1}31 : \bar{1}21$	2	14 15 - 14 16	14 15	14 16	1
$bs = 010 : \bar{1}21$	2	54 37 - 54 38	54 38	54 37	1
$so = \bar{1}21 : \bar{1}\bar{1}1$	2	21 40 - 21 47	21 43	21 44	1
$os' = \bar{1}\bar{1}1 : \bar{1}21$	2	62 44 - 62 49	62 47	62 52	5
$s'b = \bar{1}21 : 0\bar{1}0$	2	40 52 - 40 52	40 52	40 47	5
$pc = 110 : 001$	..	..	..	78 48	..
$pt = 110 : 021$	2	53 23 - 53 31	53 27	53 21	6
$to = 021 : \bar{1}\bar{1}1$	2	54 29 - 54 35	54 32	54 34	2
$op = \bar{1}\bar{1}1 : \bar{1}\bar{1}0$	2	72 0 - 72 2	72 1	72 5	4
$p'q = \bar{1}\bar{1}0 : 011$	1	..	83 58	83 52	6
$qs = 011 : \bar{1}21$	1	..	46 5	46 9	4
$sp' = \bar{1}21 : \bar{1}\bar{1}0$	1	..	49 57	49 59	2

The angles marked with an asterisk are the five angles required by triclinic symmetry as the basis of the calculations.

## CHAPTER XX

### HEXAGONAL SYSTEM

Three equal crystallographic axes lying in the same (horizontal) plane and inclined at  $60^\circ$  to each other, and a fourth (principal or vertical) axis perpendicular to them and of different length.

Characterised by a hexagonal axis of symmetry, with or without also 6 digonal axes of symmetry perpendicular to it, an equatorial plane of symmetry which contains the latter if present, and 6 symmetry planes intersecting in the hexagonal axis which then becomes dihexagonal.

THE hexagonal system bears the unique distinction of having its crystals referred to four instead of three morphological axes. It is analogous to the tetragonal system in possessing a vertical axis of special character, to which the like term of "principal axis" is given. But instead of the two equal rectangular horizontal axes lying in the equatorial plane in the case of the tetragonal system, we have now in the hexagonal system three equal axes inclined at  $60^\circ$ . The natural result of there being four axes is that there are four index numbers in the symbol of each form, namely  $\{hkl\}$ ,  $l$  referring as usual to the vertical axis.

The arrangement of the three horizontal axes is shown in Fig. 236. They are conveniently lettered  $A_1$ ,  $A_2$ , and  $A_3$ . The axis  $A_1$  is the one which emerges in front somewhat to the left, and its back half is of negative sign, the front half being positive; the axis  $A_2$  runs right-and-left parallel to the edge of the paper, and its right half is the positive one; the  $A_3$  axis runs between the  $A_1$  and  $A_2$  axes, at  $60^\circ$  to both, and its positive part is the back half, emerging towards the back-left corner of the page. The vertical axis is represented in plan by the central point. This particular arrangement of axes and of the signs of their two halves is chosen because it bears a definite and interesting relationship to the three axes of the trigonal system, which has formerly been regarded as merely a hemi-

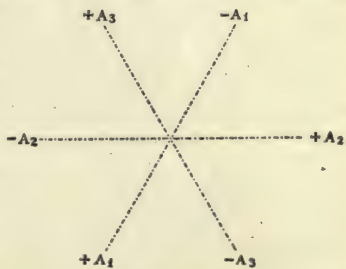


FIG. 236.

hedral form of the hexagonal system. The relationship will be discussed in Chapter XXII. in connection with the trigonal system.

Great confusion has been introduced into the description of hexagonal forms owing to the fact that no less than five different kinds of axes have from time to time been proposed and employed. The purely Millerian method referred to three axes is admirably suited to the description of trigonal forms, and in this book will be employed with and reserved for such forms, while the four-axial method above defined, suggested by Bravais and commonly known as the Bravais-Miller method, will be used for the fully hexagonal forms.

Although two out of the three equatorial axes inclined at  $60^\circ$ , together with the vertical axis, are alone adequate for the purpose of defining the position of a face, still if we refer the faces to these three axes only we are confronted with the grave disadvantage that for the three primary faces, and in general for the different faces of any one and the same form, we obtain symbols of a totally different character, incapable of being represented by a single form symbol. Thus the three primary faces would have the indices (111), ( $\bar{1}$ 01), and (0 $\bar{1}$ 1). It was only to be expected that this should be so, for the two axes would have to be quite arbitrarily chosen from amongst the three, as the latter have all the same value and are all equally entitled to be chosen. Hence, it is only by considering all three horizontal equatorial axes, together with the vertical axis, making four altogether, as the crystallographic axes, that we can obtain a form symbol capable of representing the whole of the faces of that form, the same index numbers applying to the cases of all the faces in the form. As it is highly important that faces having an equal value with reference to the symmetry of the crystal should be so represented by a single form symbol, the employment of all four Bravais-Miller axes is essential.

The elements in Bravais-Millerian hexagonal notation are thus:—

$$a : a : a : c = 1 : 1 : 1 : ?, \text{ and } \alpha = \beta = 90^\circ, \gamma = 60^\circ.$$

It is worthy of note that the sum of the three Bravais-Miller indices  $h$ ,  $i$ ,  $k$ , referring to the three horizontal axes, is always equal to zero; that is,  $h + i + k = 0$ . For instance, the hexagonal prism of the kind shortly to be described as one of the second order has the symbol  $\{11\bar{2}0\}$ , which obviously follows the rule, the sum of two positive units and *minus* two being zero. This fact is an important aid in checking the indices given to any face. Further, if two of the three indices can be found by the usual rules regarding zones, or from any other obvious considerations, the third is also given by the rule just enunciated; for it must be that number which, with the two numbers first found, makes the sum of all three = 0. A further consequence is that the signs of all these three index numbers cannot be the same.

There are five classes in the hexagonal system, four corresponding to the possible modes of combination of the symmetry elements specified at the head of the chapter, and the remaining one to the presence of the essential hexagonal axis alone. These five modes are illustrated by the five stereographic projections of the symmetry elements and of the



general form  $\{h\bar{k}l\}$  given in Figs. 237 to 241. In the first class represented in Fig. 237 (class 23) the hexagonal axis of symmetry operates alone, and this is the only one of the five classes with only a single element of symmetry. The general form here consists of a simple hexagonal pyramid. In the second class shown in Fig. 238 (class 24) the six digonal axes also operate, causing a repetition of the facial poles of the first class in the lower hemisphere, but not immediately under those of that class, being brought to the other side of the digonal axis by the rotation for  $180^\circ$ , producing a bipyramidal form of trapezohedral character. The third class is distinguished by the joint operation of the hexagonal axis and the equatorial plane of symmetry, as indicated in Fig. 239 (class 25).

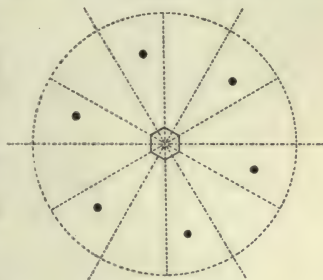


FIG. 237.—Class 23.



FIG. 238.—Class 24.

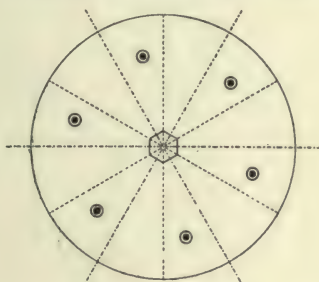


FIG. 239.—Class 25.

The general form produced thereby is the hexagonal bipyramid. In the fourth class the hexagonal axis acts dihexagonally, that is, simul-

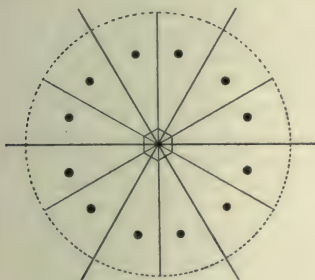


FIG. 240.—Class 26.

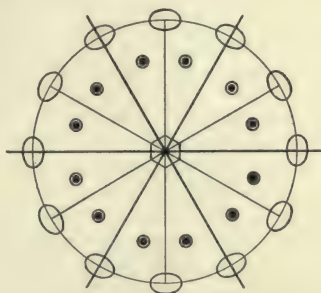


FIG. 241.—Class 27.

taneously as a hexagonal axis and in combination with six planes of symmetry intersecting in it, producing a dihexagonal pyramid, as shown in Fig. 240 (class 26). Lastly, the fifth class (class 27) combines all

the symmetry elements of the system, including of course the equatorial plane, as represented in Fig. 241, and the general form resulting has consequently poles in both hemispheres, immediately over each other, in all the positions in which poles have been shown in the other classes. This general form is the dihexagonal bipyramid.

We may now pass to the detailed consideration of these five classes.

*Class 27.—Dihexagonal-Bipyramidal Class. Beryl Class.  
Hexagonal-Holohedral Class. Type, Dihexagonal Equatorial.*

This class, just shown in stereographic projection in Fig. 241, embodies all the elements of symmetry enumerated at the beginning of the chapter, and includes all crystals which exhibit the full symmetry of the hexagonal system.

The general form, as just explained, is a 24-faced **dihexagonal bipyramid**. Its symbol is  $\{hikl\}$ , and the indices of its various faces are obtained by making all the possible interchanges of the index numbers  $h$ ,  $i$ , and  $k$ , both positive and negative, and by making  $l$  successively positive and negative also. This solid is shown in Fig. 242, the particular representative being the dihexagonal bipyramid  $\{21\bar{3}1\}$  of beryl, drawn to scale to the axial dimensions of the mineral given at the end of the description of this class. It is characterised by three different kinds of edges, namely, the equatorial edges forming the dihexagonal base, and two kinds, occurring alternately, of pyramidal (polar) edges. Of the two latter kinds, the angle over those lying in the planes which contain the vertical axis and the three respective horizontal crystallographical axes, is either acuter or more obtuse than that over those lying in the intermediate planes containing the vertical axis and the digonal interaxes, the magnitude of the angle depending on the position of the pole, in the triangle formed by two of the axes (a crystallographic one and an interaxis) radiating from the centre and the segment of the primitive circle which they cut off. When the position is as given

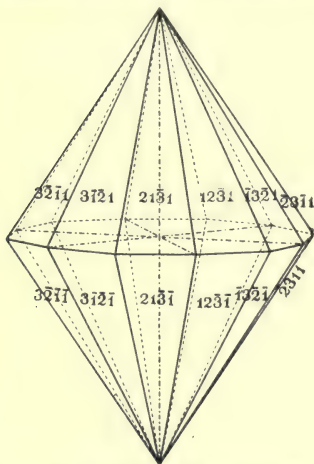


FIG. 242.—Dihexagonal Bipyramid.

in the stereographic projection in Fig. 241, the angle over the axial-plane polar edges is the more acute, but if the pole were placed nearer to the crystallographic than to the interaxis, as in the case of the dihexagonal pyramid  $\{21\bar{3}1\}$  of beryl shown in Fig. 242, the case would be reversed. The special case in which the pole would be exactly midway between the crystallographic axis and the interaxis is an impossible one, as it would render the hexagonal axis then an axis of twelve-fold symmetry, which is not possible; the indices  $hik$ , moreover, would be irrational. The only cases, therefore, corresponding to rational indices are when the pole is nearer to one or other of the axes.

When the general pole moves towards the  $30^\circ$ -angle of the triangle, that is, towards the centre, the dihexagonal bipyramid produced becomes flatter. Fig. 243 shows a combination of such a flatter bipyramid  $\{21\bar{3}2\}$  with the first one  $\{21\bar{3}1\}$  represented in Fig. 242, the  $h$ ,  $i$ , and  $k$  indices being the same but the  $l$  index number different.

The limiting case of the shortening of the vertical intercept (and corresponding increase of  $l$ ) is the **basal plane or pinakoid**  $\{0001\}$ . This primary form consists of two parallel faces, which are also shown in Fig. 243 forming the blunted ends of the bipyramid.

When the pole migrates from within the triangle on to the intersection of the primitive circle and the interaxis, we have each pair of general pyramid faces and the

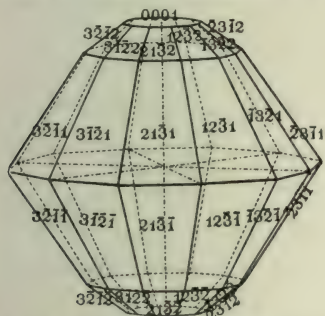


FIG. 243.—Combination of two Dihexagonal Bipyramids and Basal Pinakoid.

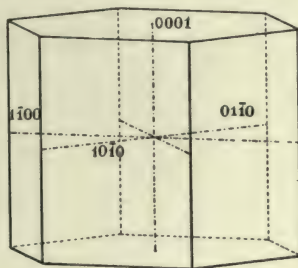


FIG. 244.—First Order Hexagonal Prism.

similar pair in the other hemisphere coalescing into a single face, parallel to the vertical axis and to one of the horizontal crystallographic axes, thus producing a hexagonal prism. Its symbol will be  $\{10\bar{1}0\}$ , and it is termed the **hexagonal prism of the first order**. It is shown in Fig. 244, closed by the two faces of the basal pinakoid.

When the pole still lies on the interaxis but not at its extremity, the corresponding **hexagonal bipyramid of the first order** is produced,  $\{h0\bar{h}l\}$ , the primary representative of which  $\{10\bar{1}1\}$  is shown in Fig. 245; the  $h$  and  $k$  indices being equal, a second  $h$  is written in the general symbol instead of  $k$ , to indicate the fact.

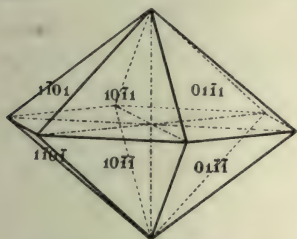


FIG. 245.—Primary First Order Hexagonal Bipyramid.

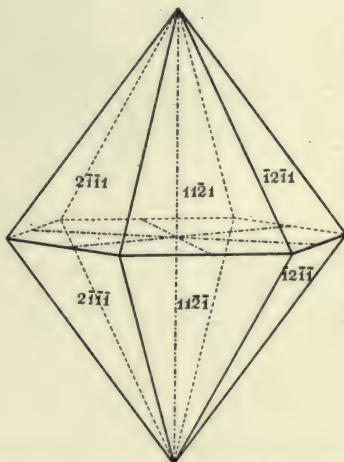


FIG. 246.—Primary Second Order Hexagonal Bipyramid.

Similarly, when the pole migrates on to a crystallographic axis, another hexagonal bipyramid is produced, and in the limiting case of the pole being situated at the intersection of that axis with the primitive circle the two faces of the bipyramid in the two hemispheres become fused into a single face of prismatic character, thus producing a second hexagonal prism. These two forms are respectively called the **hexagonal bipyramid of the second order**, and the **hexagonal prism of the second**



**order.** They are shown in Figs. 246 and 247. The symbol of the pyramid is  $\{h \cdot h \cdot 2\bar{h} \cdot l\}$  (that shown in Fig. 246 being  $\{11\bar{2}1\}$  of apatite) and of the prism  $\{11\bar{2}0\}$ . It will be obvious from the projection that the two first horizontal intercepts corresponding to the indices  $h$  and  $i$  are equal, and twice as long as the third  $k$ ; hence the indices corresponding are written as  $h \cdot h \cdot 2h$ .

There remains only one further holohedral hexagonal form to describe, namely, the **dihexagonal prism**,  $\{h\bar{i}k0\}$ , which is produced when the general dihexagonal pyramidal

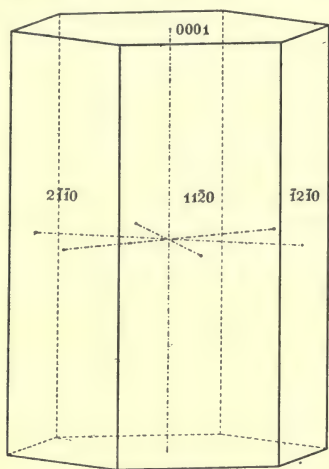


FIG. 247.—Second Order Hexagonal Prism.

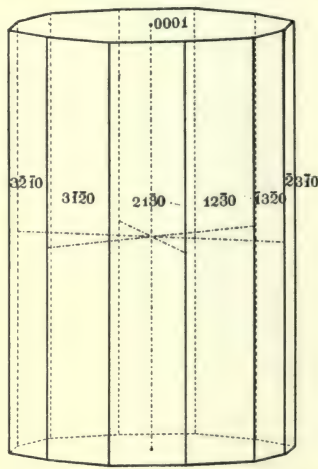


FIG. 248.—Dihexagonal Prism.

pole migrates on to the primitive circle, while still remaining in an intermediate position between the horizontal crystallographic axes and interaxes. Its section is the same as that of the dihexagonal bipyramid having the same  $h$ ,  $i$ , and  $k$  indices. Its  $\{21\bar{3}0\}$  representative is shown in Fig. 248, closed by the basal pinakoid.

These seven holohedral forms of the hexagonal system are tabulated in the following list :

*List of Forms in Class 27.*

- $\{0001\}$  Basal plane or pinakoid. 2 faces.
- $\{10\bar{1}0\}$  Hexagonal prism of the first order. 6 faces.
- $\{11\bar{2}0\}$  Hexagonal prism of the second order. 6 faces.
- $\{h\bar{i}k0\}$  Dihexagonal prism. 12 faces.
- $\{h0\bar{h}l\}$  Hexagonal bipyramid of the first order, including the primary one  $\{10\bar{1}1\}$ . 12 faces.
- $\{h \cdot h \cdot 2\bar{h} \cdot l\}$  Hexagonal bipyramid of the second order, including the primary one  $\{11\bar{2}1\}$ . 12 faces.
- $\{h\bar{i}k\bar{l}\}$  Dihexagonal bipyramid. 24 faces.

The poles of all these forms, including several representatives of each of the last three, are shown in the stereographic projection given in Fig. 249. The axial ratio used in drawing this projection was that of calcite,  $a : c = 1 : 0.8545$ . Calcite is really of trigonal symmetry, belonging to the class formerly known as the rhombohedral hemihedral division of the hexagonal system. In Chapter XXII. describing trigonal crystals, a second stereographic projection of calcite will also be given,

however, drawn according to the Millerian system of trigonal axes, and it will prove very useful to have these two projections of the same

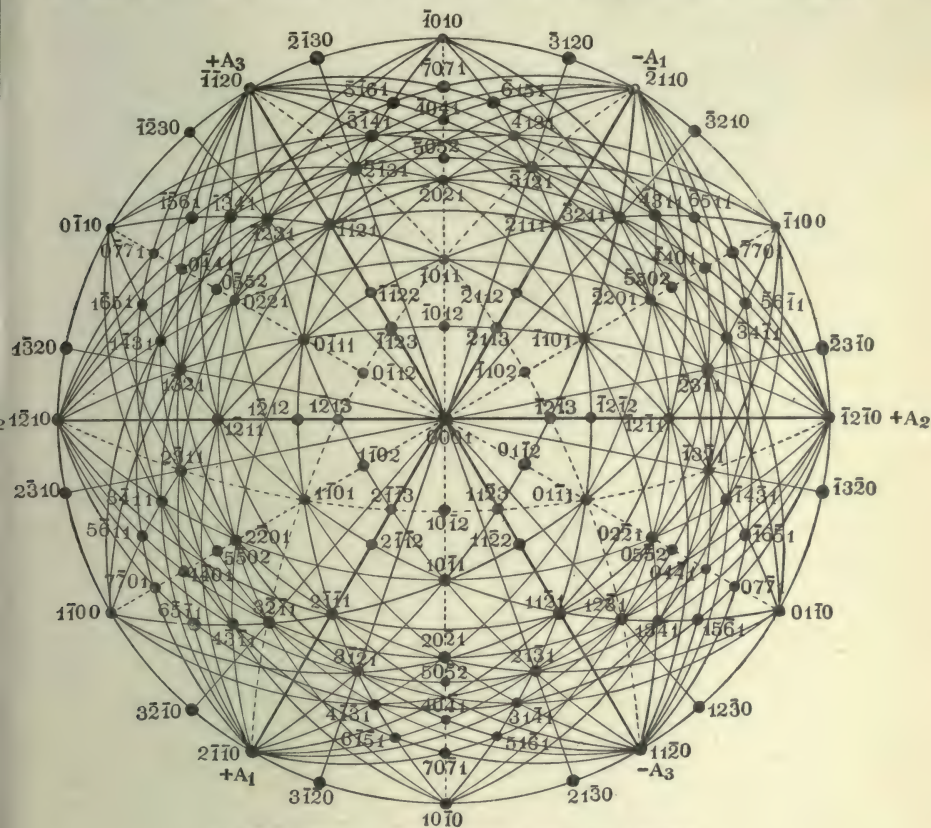


FIG. 249.—Stereographic Projection of Hexagonal Forms.

substance on the Bravais-Miller and the Millerian axial systems, in order that the corresponding two sets of indices for any one particular form may at once be compared or read off.

As regards the crystal elements, the axial angles are all known to be  $60^\circ$  or  $90^\circ$  by the conditions of the symmetry, and the three horizontal axes are of equal length. Hence the only element requiring to be found, and to be stated in connection with the description of any hexagonal crystal, is the axial ratio  $a : c$ , that of any one of the three equal horizontal axes  $a$  to the vertical axis  $c$ . This is determined by the situation of any of the pyramidal forms, and an actual example of the

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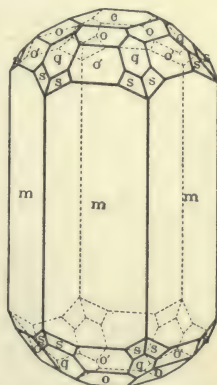


FIG. 250.—Crystal of Beryl.

X

mode of calculation, on the lines of the general instructions already given in Chapter VII., will be worked out in detail in the next chapter.

One of the best-known instances of a substance crystallising in the holohedral class of the hexagonal system is beryl,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , a typical doubly terminated crystal of which mineral is represented in Fig. 250. The forms present are  $m = \{10\bar{1}0\}$ ,  $o = \{10\bar{1}1\}$ ,  $o' = \{20\bar{2}1\}$ ,  $q = \{11\bar{2}1\}$ ,  $s = \{21\bar{3}1\}$ , and  $c = \{0001\}$ . All these forms are marked on the stereographic projection Fig. 249. The axial ratio is  $a : c = 1 : 0.4989$  (von Kokscharow). When beryl is of a pale green colour it is known as aquamarine, and when it is dark green it is the valued gem stone, the emerald. Emeralds usually exhibit cracks, these flaws aiding in the recognition and verification of the gem. The colour of aquamarine, and that also of yellow or brown beryl, is probably due to oxide of iron, and that of the emerald to oxide of chromium, held in very minute quantity in solid solution.

*Class 26.—Dihexagonal Pyramidal Class. Hexagonal-Hemimorphic Class. Type, Dihexagonal Polar.*

This class is distinguished by the intersection of six planes of symmetry mutually inclined at  $30^\circ$ , in the hexagonal (here consequently dihexagonal) symmetry axis, the vertical or principal morphological axis, as stated at the opening of the chapter, and illustrated in Fig. 251.

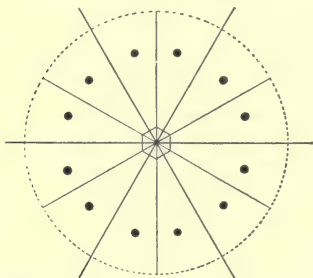


FIG. 251.—Symmetry Elements and General Form of Class 26.

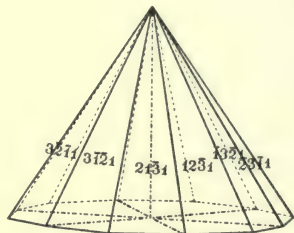


FIG. 252.—Dihexagonal Pyramid.

The operation of these symmetry elements causes the repetition of the general pole ( $hkl$ ), by reflection over the symmetry planes, eleven more times, all in the same hemisphere, thus producing the twelve-faced **dihexagonal pyramid**, shown in Fig. 252. It resembles one polar half of the dihexagonal bipyramid described in the holohedral class 27 and shown in Fig. 242, page 302, and may be closed by the basal plane.

The remarks as to the two kinds of edges and their dihedral angles, and as to the impossibility, by reason of irrationality of the indices, of a form with twelve equal dihedral angles over the polar edges and a regular twelve-sided polygon as base or section of the pyramid, apply here equally as to class 27. There are two such dihexagonal pyramids, an upper one (pointing upwards) with a positive value of the index  $l$ , and a lower one (pointing downwards) with a negative value of  $l$ .

The two basal plane faces are separate pedial forms in this class, the upper or positive pedion,  $\{0001\}$ , and the lower or negative pedion,  $\{000\bar{1}\}$ .

Similarly, when the general pole migrates on to one of the axial radii of the pro-



jection, two hexagonal pyramids are produced, an upper or positive one and a lower or negative one, and of the first or second order according as the radius on which the pole falls is an interaxis or a crystallographic axis. The sign is determined by that of the index  $l$  relating to the vertical axis.

The dihexagonal prism and the hexagonal prisms of the first and second orders are identical with those of class 27, for they are the limiting cases of both the positive and negative pyramidal forms, when the poles have migrated on to the primitive circle.

There are to be distinguished in this class, therefore, the following forms :

*List of Forms in Class 26.*

- $\{0001\}$  Upper or positive basal plane or pedion ;  $\{000\bar{1}\}$  lower or negative basal plane or pedion. 1 face each.
- $\{10\bar{1}0\}$  Hexagonal prism of the first order. 6 faces.
- $\{11\bar{2}0\}$  Hexagonal prism of the second order. 6 faces.
- $\{h\bar{k}0\}$  Dihexagonal prism. 12 faces.
- $\{h0\bar{h}l\}$  Upper or positive hexagonal pyramid of the first order ;  $\{h0\bar{h}\bar{l}\}$  lower or negative pyramid of the first order. Including the primary ones  $\{10\bar{1}1\}$  and  $\{10\bar{1}\bar{1}\}$ . Each 6 faces.
- $\{h.h.\bar{2}h.l\}$  Upper or positive hexagonal pyramid of the second order ;  $\{h.h.\bar{2}h.\bar{l}\}$  lower or negative hexagonal pyramid of the second order. Including the primary ones  $\{11\bar{2}1\}$  and  $\{11\bar{2}\bar{1}\}$ . Each 6 faces.
- $\{h\bar{k}l\}$  Upper or positive dihexagonal pyramid ;  $\{h\bar{k}\bar{l}\}$  lower or negative dihexagonal pyramid. Each 12 faces.

An instance of a substance crystallising according to this class of symmetry is the naturally occurring sulphide of cadmium, greenockite,  $\text{CdS}$ . Fig. 253 shows a typical crystal of greenockite consisting of the hexagonal prism  $\{10\bar{1}0\}$ , the two basal planes  $\{0001\}$  and  $\{000\bar{1}\}$  developed to very different extents, and the four pyramids (two only of which are complementary forms)  $\{02\bar{2}1\}$ ,  $\{10\bar{1}1\}$  and  $\{10\bar{1}\bar{1}\}$ , and  $\{10\bar{1}2\}$ . The axial ratio is  $a:c=1:0.8252$ . The poles of all these forms are indicated on the stereographic projection in Fig. 249, and although for a crystal of the axial dimensions of calcite, the relative positions of the forms are similar.

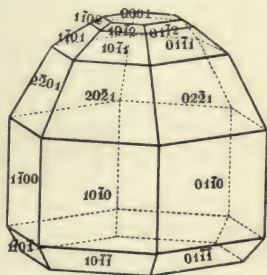


FIG. 253.—Crystal of Greenockite.

*Class 25.—Hexagonal Bipyramidal Class. Apatite Class. Pyramidal-Hemihedral Class. Type, Hexagonal Equatorial.*

In this class the operating symmetry elements are the essential hexagonal axis and the equatorial plane of symmetry.

From the stereographic projection, Fig. 254, it will be clearly apparent that the general pole  $\{h\bar{k}l\}$  is repeated five times owing to the operation of the hexagonal axis, making a hexagonal pyramid, and each of these six poles in the upper hemisphere is repeated vertically underneath in the lower hemisphere, by virtue of the operation of the equatorial plane of symmetry, converting the pyramid into a bipyramid. To distinguish this hexagonal bipyramid from the holohedral ones of the first and second orders, it is termed a **hexagonal bipyramid of the third order**,

as in the case of the analogous tetragonal bipyramid of the third order belonging to class 12. This third order hexagonal bipyramid is shown in Fig. 255. The actual representative shown is the form  $\{21\bar{3}1\}$  constructed to scale to the axial ratio of apatite  $a : c = 1 : 0.7345$ , a mineral which shows the form characteristically. There will be a second similar form possible, having the same index numbers, corresponding to the other six poles shown in the holohedral Fig. 241. The first form  $\{h\bar{k}l\}$  (Fig. 255) is distinguished as the **right hexagonal bipyramid of the third order**, and the second form, indistinguishable as a separate solid from the first, has the indices  $\{k\bar{h}l\}$  and is termed the **left hexagonal bipyramid of the third order**.

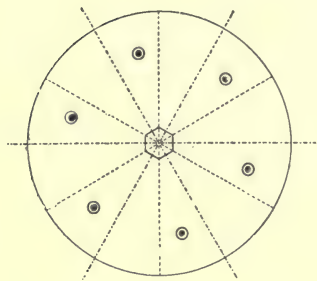


FIG. 254.—Symmetry Elements and General Form of Class 25.

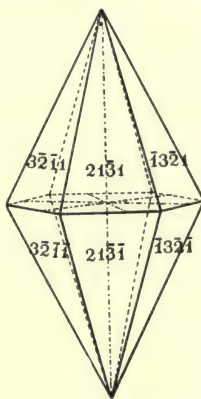


FIG. 255.—Right Third Order Hexagonal Bipyramid.

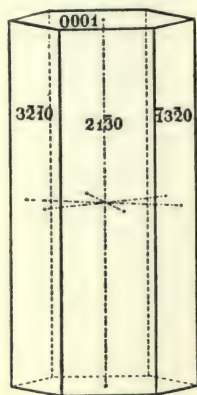


FIG. 256.—Right Third Order Hexagonal Prism.

The first and second order hexagonal bipyramids form the limiting cases of both right and left third order forms, when the poles coalesce on the radial axes.

Three orders of prisms naturally correspond to these three orders of hexagonal bipyramids. Those of the first and second orders are identical with the holohedral class 27 forms, but the **hexagonal prism of the third order** exhibits two varieties, a **right** and a **left**, corresponding to the two third order bipyramids. The right form is  $\{h\bar{k}0\}$ , and the left form  $\{k\bar{h}0\}$ . The right hexagonal prism of the third order  $\{2130\}$  of apatite, corresponding to the right bipyramid  $\{21\bar{3}1\}$  of Fig. 255, is shown in Fig. 256, drawn to scale in equipose and terminated by the basal pinakoid  $\{0001\}$ . This latter form, the basal pinakoid, remains as in the holohedral class 27.

There are, consequently, to be distinguished the following forms in this class :

#### *List of Forms in Class 25.*

- $\{0001\}$  Basal pinakoid. 2 faces.
- $\{10\bar{1}0\}$  Hexagonal prism of the first order. 6 faces.
- $\{11\bar{2}0\}$  Hexagonal prism of the second order. 6 faces.
- $\{h\bar{k}0\}$  Right hexagonal prism of the third order;  $\{k\bar{h}0\}$  left hexagonal prism of the third order. Each 6 faces.
- $\{h0hl\}$  Hexagonal bipyramid of the first order, including the primary one,  $\{10\bar{1}1\}$ , 12 faces.
- $\{h . h . 2\bar{h} . l\}$  Hexagonal bipyramid of the second order, including the primary one  $\{11\bar{2}1\}$ . 12 faces.
- $\{h\bar{k}l\}$  Right hexagonal bipyramid of the third order;  $\{k\bar{h}l\}$  left hexagonal bipyramid of the third order. Each 12 faces.

An excellent example of a substance crystallising in class 25 is the natural mineral apatite,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$  or  $\text{Ca}_5\text{Cl}(\text{PO}_4)_3$ . A typical crystal of apatite will be worked through goniometrically in the next chapter, its axial ratio calculated, and the mode of carrying out hexagonal calculations in general thereby exemplified. According to F. Rinne<sup>1</sup> ice crystallises in this hexagonal-bipyramidal class, the ratio of the axes being  $a : c = 1 : 1.678$ , very clear evidence being afforded by X-ray photographs with ice-plates parallel to the basal plane. Von Groth<sup>2</sup> considers ice to belong to the ditrigonal pyramidal class of the trigonal system, class 20.

*Class 24.—Hexagonal Trapezohedral Class. Trapezohedral-Hemihedral Class. Type, Hexagonal Holoaxial.*

The symmetry elements present in this class, as the type implies, are the full number of axes of symmetry belonging to the system, namely, the hexagonal axis and the 6 digonal axes perpendicular thereto lying in the equatorial plane. But this latter plane is no longer a plane of symmetry, nor are any planes of symmetry whatever present.

The mode of repetition of the general pole  $\{hik\bar{l}\}$ , by passing from one hemisphere to the other alternately, will be clear from Fig. 257. The hexagonal axis causes the repetition of the pole five more times at  $60^\circ$ -intervals round the circle in the same hemisphere, and the digonal character of each of the 6 axes of symmetry in the equatorial plane causes each pole to be again repeated in the other hemisphere, not vertically under the pole in the upper hemisphere, but instead, at the same distance on the other side of the axis, as projected. It is as if alternate poles in the holohedral projection in Fig. 241 had been suppressed, the dot being removed from one double pole and the ring from the adjoining one. The effect is to produce a hexagonal bipyramid of the third order, but of which the two halves (single pyramids), upper and lower, belong respectively to the right and the left forms described in Class 25. That is, the two pyramids are not congruent, one being rotated round the vertical axis somewhat with respect to the other, so that each of the edges of the usual hexagonal basal plane section is replaced by a pair of unequal shorter edges, so arranged that the twelve form a zig-zag around the wide middle belt of the bipyramid. Each face of the solid is thus bounded by four edges, two equal polar and two unequal equatorial, rendering it a trapezohedron.

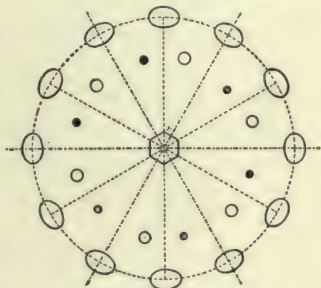


FIG. 257.—Symmetry Elements and General Form of Class 24.

It will be obvious that there must be two enantiomorphous hexagonal trapezohedra corresponding to the same index numbers, a **right** one  $\{hik\bar{l}\}$ , so called because the faces of the right upper hexagonal pyramid of the third order form the upper half, and which is represented in Fig. 258 and by its poles in Fig. 257; and a **left** one  $\{k\bar{i}hl\}$ , shown in Fig. 259, and the upper faces of which are formed by the left upper hexagonal pyramid of the third order. The pair shown in Figs. 258 and 259 are the right and left trapezohedra  $\{21\bar{3}1\}$  and  $\{3\bar{1}21\}$ , the axial ratio employed in the drawing being that of apatite. These two forms distinguish the class, all the remaining forms being

<sup>1</sup> Ber. k. Sachs. Ges. Wiss., math.-phys. Klasse, 1917, 69, 57.

<sup>2</sup> Chemische Krystallographie, vol. i. p. 66.



identical with those of the holohedral class 27. For all these other forms correspond to the six special cases, in which the pole is no longer a general one within the spherical triangle formed by two radii and a twelfth-part segment of the primitive circle, but lies on one of the six elements of the triangle, that is, either on one of the arc-sides or at one of the corner-angles formed by their intersection. In all these cases the effect of the axial elements of symmetry alone is to produce the holohedral forms. When the pole is at the central corner the basal pinakoid is produced, when at the end of an interaxis the first order hexagonal prism is formed, and when at the end of a crystallographic axis the second order prism is developed. Its position on the primitive circle segmental side-arc of the triangle gives rise to the dihexagonal prism,

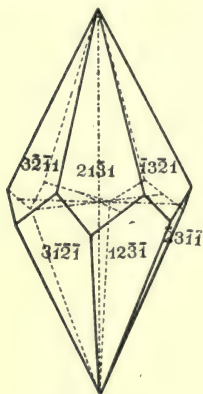


FIG. 258.  
Right and Left Hexagonal Trapezohedra.

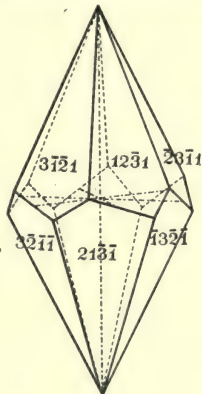


FIG. 259.

when located on an interaxial arc (radius in the projection) the first order hexagonal bipyramid is arrived at, and when on a crystallographic axial arc the second order bipyramid is the form brought about.

Hence there are the following forms comprised in this class :

*List of Forms in Class 24.*

- {0001} Basal pinakoid. 2 faces.
- {1010} Hexagonal prism of the first order. 6 faces.
- {1120} Hexagonal prism of the second order. 6 faces.
- {hik0} Dihexagonal prism. 12 faces.
- {h0hl} Hexagonal bipyramid of the first order, including the primary one {1011}. 12 faces.
- {h . h . 2h . l} Hexagonal bipyramid of the second order, including the primary one {1121}. 12 faces.
- {hikl} Right hexagonal trapezohedron ; {kih1} left hexagonal trapezohedron. Each 12 faces.

Examples of this class are uncommon. The best-known is that of the complex double salt barium antimonyl tartrate with potassium nitrate,  $\text{Ba}(\text{SbO})_2(\text{C}_4\text{H}_4\text{O}_6)_2 \cdot \text{KNO}_3$ . The forms exhibited by this salt, however, do not display the trapezohedral character of the symmetry, being the holohedral forms {1010}, {0001}, {1011}, and {2021}. But the etched figures afforded by small quantities of water exhibit very clearly the presence of digonal axes and the absence of a symmetry plane.

*Class 23.—Hexagonal Pyramidal Class. Hexagonal-Hemimorphic-Hemihedral Class. Type, Hexagonal Polar.*

This class exhibits the minimum of hexagonal symmetry, namely, nothing but the essential hexagonal axis of symmetry. This, the vertical and crystallographically principal axis, is consequently one of hemimorphism, for the forms developed at its two ends may be different, there

being neither equatorial plane of symmetry nor digonal axes of symmetry lying in it.

The pole of any face whatsoever is simply repeated at every  $60^\circ$  symmetrically round the hexagonal vertical axis, so that in general,—the starting pole not lying on any one of the six elements of the spherical triangle (formed in the projection by an interaxial radius, an adjacent crystallographic radius, and the segment cut off by them on the primitive circle) but within the triangle,—the form produced is a simple hexagonal pyramid of the third order, upper or lower according to the hemisphere. Its projection is shown in Fig. 260, and its appearance, as closed by the basal plane, is represented in Fig. 261, the actual one drawn being the right upper hexagonal

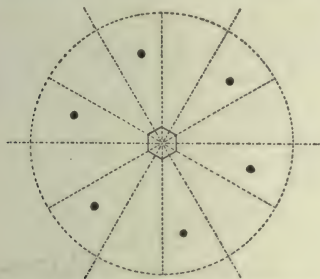


FIG. 260.—Symmetry Element and General Form of Class 23.

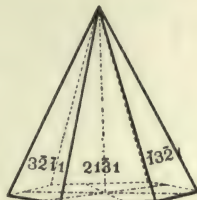


FIG. 261.—Right Upper Third Order Hexagonal Pyramid.

pyramid of the third order  $\{21\bar{3}1\}$ , corresponding to the upper half of Fig. 255. For, besides the two forms, upper and lower, corresponding to the two ends of the hexagonal axis, there will be another pair of forms enantiomorphous with them, the two pairs being right and left respectively and having the same index numbers; the poles of the second form will lie on the other side of the interaxis in each case, and at the same distance from it as the poles of the first form (shown in the projection and drawing). The latter is a right form, and the enantiomorphous second form is the left one. Hence, four general forms are altogether to be distinguished in this class, as together making up the 24-faced holohedral dihexagonal bipyramid of class 27.

Of the six special cases, the only ones which remain as in the holohedral class are the first and second order hexagonal prisms, produced when the poles fall at the ends of the two kinds of axes. The two pyramids, first and second order, are only simple pyramids, either upper or lower, and not bipyramids, so that each of the holohedral bipyramids is now divided into an upper and a lower form, differing by the sign of the  $l$  index. Similarly, the holohedral basal pinakoid is now divided into two basal planes or pedions, an upper or positive  $\{0001\}$  and a lower or negative  $\{000\bar{1}\}$ . When the general pole falls on the primitive-circle-segment side of the triangle two varieties of hexagonal prism of the third order are produced, just as in class 25, a right and a left modification, according as the pole is to the right or the same distance to the left of the interaxis.

To summarise, we have to distinguish the following forms in the class :

*List of Forms in Class 23.*

- $\{0001\}$  Upper or positive basal plane or pedion ;  $\{000\bar{1}\}$  lower or negative basal plane or pedion. Each 1 face.
- $\{10\bar{1}0\}$  Hexagonal prism of the first order. 6 faces.
- $\{11\bar{2}0\}$  Hexagonal prism of the second order. 6 faces.
- $\{h\bar{k}l0\}$  Right hexagonal prism of the third order ;  $\{k\bar{h}l0\}$  left hexagonal prism of the third order. Each 6 faces.

$\{h0\bar{h}l\}$  Upper or positive hexagonal pyramid of the first order;  $\{h0\bar{h}\bar{l}\}$  lower or negative hexagonal pyramid of the first order. Including the primary pyramids  $\{10\bar{1}1\}$  and  $\{10\bar{1}\bar{1}\}$ . Each 6 faces.

$\{h.h.2\bar{h}.l\}$  Upper or positive hexagonal pyramid of the second order;  $\{h.h.2\bar{h}.\bar{l}\}$  lower or negative hexagonal pyramid of the second order. Including the primary pyramids  $\{11\bar{2}1\}$  and  $\{11\bar{2}\bar{1}\}$ . Each 6 faces.

$\{h\bar{k}l\}$  Right upper or positive hexagonal pyramid of the third order;  $\{k\bar{i}h\}$  left upper or positive form of same;  $\{h\bar{k}\bar{l}\}$  right lower or negative hexagonal pyramid of the third order;  $\{k\bar{i}\bar{h}\bar{l}\}$  left lower or negative form of same. Each 6 faces.

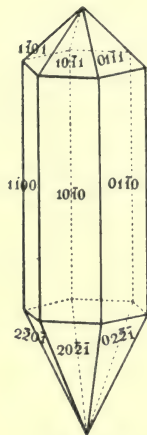


FIG. 262.  
Crystal of Strontium  
Antimonyl Tartrate.

An excellent example of this class is afforded by the salt strontium antimonyl tartrate,  $\text{Sr}(\text{SbO})_2(\text{C}_4\text{H}_4\text{O}_6)_2$ , investigated by Traube, a crystal of which is shown in Fig. 262. The hemimorphic pyramidal character is at once displayed in the different forms developed at the two ends of the hexagonal prism  $\{10\bar{1}0\}$  of the first order, the predominating form. At the upper end is the primary positive hexagonal pyramid of the first order  $\{10\bar{1}1\}$ , while the lower termination is formed by the entirely different first order pyramid  $\{20\bar{2}\bar{1}\}$ . The etched figures on the prism faces confirm the fact that the crystal belongs to this class, as does also the circumstance that the two poles exhibit strongly opposite pyroelectric properties. The upper pole is the antilogous pole and the lower one the analogous.



## CHAPTER XXI

### PRACTICAL EXAMPLE OF A HEXAGONAL CRYSTAL

*Class 25.—Apatite,  $Ca_5F(PO_4)_3$  or  $Ca_5Cl(PO_4)_3$ .*

THE example chosen as illustrative of the mode of dealing with crystals of the hexagonal system is a beautiful little crystal of apatite of prismatic habit, perfectly transparent and colourless, and very rich in faces. It is about three millimetres long and just over a millimetre in the diameter of the prism. One end only is fully developed, the crystal having been attached to a cavity wall by the other end. But on the free end twenty-four faces are developed, making thirty-six faces altogether, including the prism faces.

Investigation showed that the basal pinakoid was prominently represented by the broad flat-end plane (0001), marked *c* on the reproduced drawing given in Fig. 263; the crystal was so evenly developed that this basal plane was almost a regular hexagon. Its six edges were parallel to the three Bravais-Miller horizontal axes, and to the faces of the hexagonal prism of the first order,  $m=\{10\bar{1}0\}$ , and to those of the first order hexagonal pyramid  $o'=\{20\bar{2}1\}$ , which were the two other most prominent forms developed on the crystal, the pyramid faces intervening as replacing or sharpening facets between the prism and the basal plane. The prism was the most largely developed, conferring on the crystal its prismatic habit. But besides these three predominating forms there were four others present, three of them forming numerous additional little facets of great brilliancy about the termination. They consisted of faces of the primary first order pyramid  $o=\{10\bar{1}1\}$ , of the first order pyramid  $o''=\{10\bar{1}2\}$ , and of the primary pyramid of the second order  $q=\{11\bar{2}1\}$ . The fourth of these forms was the hexagonal prism of the second order,  $n=\{11\bar{2}0\}$ , narrower faces of which replaced the edges of intersection of the broader faces of the prism of the first order *m*.

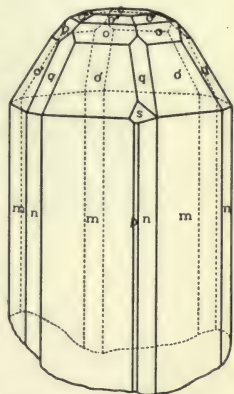


FIG. 263.—Measured Crystal of Apatite.

The whole of these seven forms, practically all the faces of which

were present and afforded brilliant reflections in spite of the very minute size of some of them, are identical with the holohedral forms of class 27 of the hexagonal system, the class which exhibits the full symmetry of the system. There were also present, however, two very small faces of the forms  $s=\{21\bar{3}1\}$ , a right hexagonal pyramid of the third order, and  $p=\{21\bar{3}0\}$ , a right hexagonal prism of the third order, both of which are illustrated on page 308, Figs. 255 and 256. The light reflected from them, however, was too feeble to permit of satisfactory measurements, although adequate for the purpose of identification and the determination of their approximate positions. It is the frequent presence of either or both of these forms on crystals of the mineral which determines that apatite belongs to class 25, the so-called pyramidal-hemihedral class of the hexagonal system according to the older method of classification, or according to our new and better-based structural method, the hexagonal bipyramidal or hexagonal equatorial class, fully dealt with in the preceding chapter. The chief points of difference from the holohedral class 27 are that the dihexagonal prism and dihexagonal bipyramid are each divided into two forms, a right and a left hexagonal prism or bipyramid of the third order, which are not necessarily or even usually present on the same crystal. The right bipyramid  $s=\{21\bar{3}1\}$  is characteristic of apatite, and the corresponding right prism  $p=\{21\bar{3}0\}$  is also not infrequently present on crystals of the mineral.

The prism zone is obviously the one with which to commence the goniometrical measurements.

Fixing the crystal upright on the wax of the crystal holder, on adjusting two faces of the zone to the axis of the goniometer, the whole twelve faces constituting the zone are found to be also automatically adjusted in accordance with the chief property of a zone. There are six broad faces of the first order prism  $m$ , and one broad and five narrow faces of the second order prism  $n$ . All seven broad faces gave excellent "A" reflections of the signal-slit of the goniometer, and all but one of the narrower  $n$  faces also gave good images of the signal, although not so brilliant as the seven just mentioned. The actual measurements obtained on the Fuess horizontal circle goniometer were as follows:

#### PRISM ZONE OF APATITE.

Circle Readings.	Angles.	
	<i>mn.</i>	<i>mm.</i>
<i>m</i> 360° 0' A	29° 56'	
<i>n</i> 330 4	29 59	59° 55' A
<i>m</i> 300 5 A	30 5	
<i>n</i> 270 0	30 0	60 5 A
<i>m</i> 240 0 A	29 58	
<i>n</i> 210 2	29 56	59 54 A
<i>m</i> 180 6 A	30 4 A	
<i>n</i> 150 2 A	29 59 A	60 3 A
<i>m</i> 120 3 A	29 56	
<i>n</i> 90 7	30 4	60 0 A
<i>m</i> 60 3 A	29 58 A	
<i>n</i> 30 5 A	30 3 A	60 1 A
<i>m</i> 0 2 A		

A careful inspection of this table of measurements convinces us that the zone is that of a hexagonal or trigonal crystal. The whole of the values of the angles between adjacent  $m$  and  $n$  faces are within  $5'$  of  $30^\circ$ , and those of the angles of the first order prism  $mm$  are within  $6'$  of  $60^\circ$ . Now this is a case where it is useless and positively misleading to take the mean of all the  $mm$ ,  $mn$  or  $nn$  values, for they would obviously be bound to work out exactly to  $60^\circ$ ,  $30^\circ$ , and  $60^\circ$  respectively, as in each case it is equivalent to dividing  $360^\circ$  by 6 or 12. When the whole of the angles in a zone are nearly alike, the method of taking the mean is not legitimate, for the round figure for the aliquot part of the circle is bound to be the result of the operation. The only safe thing to do is to rely on the best "A" individual values as indicating the truth, and also to consider these in connection with the measurements of other zones, which will aid in arriving at the true symmetry, and also finally, if the substance be a transparent one, in connection with the optical investigation of the crystal, which is sure to afford additional and unmistakable evidence of a decisive character as to the system of symmetry to which the crystal belongs, and which will be fully dealt with in later chapters of this book (Part III.). If this crystal of apatite were not of truly hexagonal symmetry, which would correspond to the possession of a single optic axis along which there would be no double refraction, and which would be identical with the direction of the principal, hexagonal, axis of symmetry, it would belong to one of the systems, probably the rhombic, which possess two optic axes; and as optically uniaxial and biaxial crystals exhibit very clearly their single axis or their two optic axes, surrounded by circular interference rings in the one case, and by rings and loop-like or ellipse-like lemniscates in the other, when examined in convergent polarised light, there could be no possible ambiguity.

An excellent example of a rhombic crystal which exhibits in the prism zone a very close approximation to hexagonal symmetry, the prism angles being within a quarter of a degree of  $30^\circ$ , has already been discussed in the case of the typical crystal of potassium sulphate, in Chapters IV. and VIII. In that case, however, which is one of the best known and nearest to perfect hexagonality, the true exact (final mean) differences from  $30^\circ$  were  $12'$ , the angles in each quadrant being  $30^\circ 12'$ ,  $30^\circ 0'$ , and  $29^\circ 48'$  respectively, an amount quite outside possible experimental error. On the other hand, in the case of apatite, the maximum apparent difference is only  $6'$  irregularly distributed, and the difference almost entirely disappears if we take the mean of the angular values derived from parallel faces, which is quite legitimate, as there is absolutely no doubt that these faces were intended to be truly parallel. That is, if we take the mean of the first and fourth values of  $mm$  (which gives  $59^\circ 59'$ ), of the second and fifth ( $60^\circ 2'$ ), and of the third and sixth ( $59^\circ 58'$ ), we have three legitimate values which lie at a maximum of  $2'$  on both sides of  $60^\circ$ , and which therefore indicate that the endeavour of the growing crystal was to produce faces inclined truly at  $60^\circ 0'$ , the minute difference being undoubtedly due to slight disturbance during growth. It would not be legitimate, however, to take the mean



of the first three values of  $mm$ , or of the last three, or of the three mean values just given, as evidence of hexagonal symmetry; it is rather the fact of the closeness to within  $2'$  of the three individual values in each of the two parallel sets which indicates the probability of such hexagonal symmetry.

Similarly, if we take the mean of the  $mn$  angles formed by parallel  $m$  and parallel  $n$  faces, beginning with the mean of the first and seventh and finishing with the mean of the sixth and twelfth, we obtain six legitimate mean values for  $mn$ , namely,  $30^\circ 0'$ ,  $29^\circ 59'$ ,  $30^\circ 1'$ ,  $30^\circ 2'$ ,  $29^\circ 58'$ , and  $30^\circ 0'$ , the maximum difference among which is again only  $2'$ , which is within the limits of error or malformation for the very best of crystals. The true angle  $mn$  can, therefore, be accepted as  $30^\circ 0'$ . The difference of  $12'$  in the case of the rhombic potassium sulphate is fairly comparable to this, for it was the mean result derived from numerous strictly legitimate "A" values afforded by eleven different excellent crystals, each of such values corresponding to the specific angle in the quadrant only, that is, to the proper one of the three. There can, therefore, be no hesitation in concluding that the symmetry of apatite is truly hexagonal, while that of potassium sulphate is only pseudo-hexagonal, and in reality rhombic, the angle  $30^\circ 12'$  being repeated four times in such positions in the zone as are consonant with the symmetry of that system. These conclusions are fully borne out by the optical properties, apatite showing a single optic axis in the direction of the vertical axis, the axis of the zone in question and that of hexagonal symmetry, while potassium sulphate is optically biaxial.

The point which has just been discussed at some length is of supreme importance, or so much space would not have been devoted to it. It is perhaps the chief pitfall into which a beginner in crystallographic measurement may precipitate himself. It is so easy, when a zone of angles verging on  $30^\circ$  or  $60^\circ$  is discovered on a crystal, to take the mean and obtain exactly  $30^\circ 0'$  or  $60^\circ 0'$  as the result, and to jump immediately to the conclusion that a hexagonal crystal is in question. For pseudo-hexagonal crystals are by no means uncommon; indeed Fedorov has concluded that all crystals are either pseudo-hexagonal or pseudo-cubic (but within very considerably wider limits than the above) when they are not truly hexagonal or cubic. A word of emphatic caution is thus necessary against arriving at hasty conclusions as to the system of symmetry to which a crystallised substance belongs. An investigator of ripe experience almost completes his exhaustive series of goniometrical and optical measurements and observations before he feels justified in finally stating a definite conclusion as to the system and class of symmetry.

We may now pass on to the measurement of other zones on the crystal of apatite. The next in order of importance are those perpendicular to the one already measured. This latter, the prism zone, may at once be graphically exhibited on the primitive circle of the stereographic projection, the poles being arranged at  $30^\circ$  from each other, as shown in Fig. 264. The centre of the circle represents the vertical hexagonal axis in plan, and the pole situated there is that of the basal plane  $c = (0001)$ . If we now draw diameters joining opposite prism poles  $mm$  and  $nn$ , we have the projection of six zones perpendicular to the prism zone, three similar ones being represented by those

diameters which indicate the directions of the Bravais-Miller axes, marked in Fig. 264 by greater strength of line, and three other zones different from the above but like each other, represented by the interaxial diameters.

It will be convenient first to proceed to the measurement of the three latter zones. For the crystal is set up, both in the drawing of Fig. 263 and in the stereographic projection, Fig. 264, with the broad *m*-faces arranged as is usual for the prism of the first order, namely, so that one of these *m*-faces is in front, parallel to the right-and-

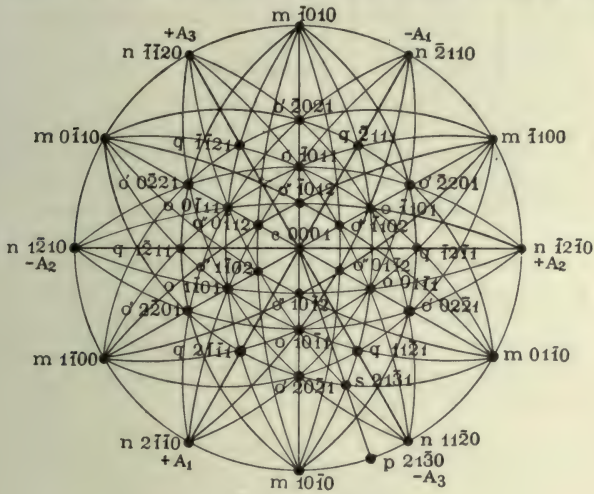


FIG. 264.

left Bravais-Miller axis (horizontal in the projection) and perpendicular to the back-and-front interaxis (vertical in the projection). The larger pyramidal faces are those in the zone [*mcm*], and it is these three similar [*mcm*] zones indicated in the projection by the interaxial diameters that we shall next proceed to measure. The crystal is set up for the purpose horizontally on the wax of the crystal holder, and with an *m*-face and a *c*-face respectively arranged approximately parallel to the two tangent screws of the adjusting movements of the goniometer. On effecting the fine adjustment of these two faces to the axis of the goniometer in the usual manner, with the aid of the two adjusting and two centring movements, there are found to be also automatically adjusted, as belonging to the zone, the other parallel *m*-face, and between *m* and *c* on each side of the latter, a face of each of the pyramids *o*, *o'*, and *o''*.

The following measurements were obtained from the three such zones present on the crystal :

3 ZONES [*mcm*].

Circle Readings.	Angles.	Circle Readings.	Angles.
$\left\{ \begin{array}{l} m \ 360^{\circ} \ 0' A \\ o' \ 329 \ 29 \\ o \ 310 \ 15 \\ e \ 270 \ 0 A \\ o'' \ 247 \ 2 A \\ o \ 229 \ 40 A \\ o' \ 210 \ 30 A \\ m \ 179 \ 59 A \end{array} \right.$	$\left\{ \begin{array}{l} mo' \ 30^{\circ} \ 31' \\ o'o \ 19 \ 14 \\ oc \ 40 \ 15 \\ co'' \ 22 \ 58 A \\ o''o \ 17 \ 22 A \\ oo' \ 19 \ 10 A \\ o'm \ 30 \ 31 A \end{array} \right.$	$\left\{ \begin{array}{l} m \ 360^{\circ} \ 0' A \\ o' \ 329 \ 29 A \\ o \ 310 \ 20 A \\ c \ 270 \ 2 A \\ o'' \ 247 \ 1 A \\ o \ 229 \ 46 \\ o' \ 210 \ 32 A \\ m \ 180 \ 0 A \end{array} \right.$	$\left\{ \begin{array}{l} mo' \ 30^{\circ} \ 31' A \\ o'o \ 19 \ 9 A \\ oc \ 40 \ 18 A \\ co'' \ 23 \ 1 A \\ o''o \ 17 \ 15 \\ oo' \ 19 \ 14 \\ o'm \ 30 \ 32 A \end{array} \right.$

Circle Readings.	Angles.
$\left\{ \begin{array}{l} m \ 360^\circ \ 0' A \\ o' \ 329 \ 30 \ A \\ o \ 310 \ 20 \ A \\ o'' \ 292 \ 56 \\ c \ 270 \ 0 \ A \\ o'' \ 247 \ 1 \ A \\ o \ 229 \ 41 \\ o' \ 210 \ 30 \ A \\ m \ 179 \ 59 \ A \end{array} \right.$	$\left\{ \begin{array}{l} mo' \ 30^\circ \ 30' A \\ o'o \ 19 \ 10 \ A \\ oo'' \ 17 \ 24 \\ o''c \ 22 \ 56 \\ co'' \ 22 \ 59 \ A \\ o'o \ 17 \ 20 \\ oo' \ 19 \ 11 \\ o'm \ 30 \ 31 \ A \end{array} \right.$
	$\left\{ \begin{array}{l} oc \ 40^\circ \ 20' A \\ co \ 40 \ 19 \end{array} \right.$

It will be obvious that the angles are symmetrically arranged on each side of the basal plane  $c$ . The values of like angles may be collected together and the means taken. The proof of the symmetry lies, however, in the fact that the "A" values of similar angles on the two sides of  $c$  are so nearly absolutely identical, that the differences are within the range of error or malformation exhibited even by the best crystals; the values of  $mo'$ , for instance, are all identical within  $2'$ , a range of error which is certainly permissible in the values of angles intended to be actually identical. The mean values are:  $mo' = 30^\circ 31'$ ,  $o'o = 19^\circ 11'$ ,  $oo'' = 17^\circ 20'$ ,  $o''c = 22^\circ 59'$ , and  $oc = 40^\circ 18'$ .

We pass next to the measurement of the three other equal zones, the projections of which are the Bravais-Miller axial diameters, namely, the zones  $[ncn]$ , the crystal being again fixed horizontally on the wax, but rotated about its axis so as to get each of the three zones in turn adjusted, as in the case of the three zones just measured. When any  $n$ -face and the basal plane  $c$  are adjusted parallel to the movements and then finally to the axis, and properly centred, it is found that a second (the parallel)  $n$ -face is also adjusted, and also two  $q$ -faces, one on each side of  $c$ . The result of the measurements actually obtained is given below.

### 3 ZONES $[ncn]$ .

Circle Readings.	Angles.	Circle Readings.	Angles.	Circle Readings.	Angles.
$\left\{ \begin{array}{l} n \ 360^\circ \ 0' A \\ q \ 325 \ 43 \ A \\ c \ 269 \ 59 \\ q \ 214 \ 11 \ A \\ n \ 179 \ 57 \ A \end{array} \right.$	$\left\{ \begin{array}{l} nq \ 34^\circ \ 17' A \\ qc \ 55 \ 44 \\ cq \ 55 \ 48 \\ qn \ 34 \ 14 \ A \end{array} \right.$	$\left\{ \begin{array}{l} n \ 360^\circ \ 0' A \\ q \ 325 \ 44 \ A \\ c \ 270 \ 0 \\ n \ 180 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} nq \ 34^\circ \ 16' A \\ qc \ 55 \ 44 \\ cn \ 90 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} n \ 360^\circ \ 0' A \\ q \ 325 \ 45 \ A \\ c \ 269 \ 59 \ A \\ n \ 180 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} nq \ 34^\circ \ 15' A \\ qc \ 55 \ 46 \ A \\ cn \ 89 \ 59 \end{array} \right.$

We may collect the four values of each of the angles  $nq$  and  $qc$ , and extract their mean values, which prove to be  $nq = 34^\circ 15'$  and  $qc = 55^\circ 45'$ . For we are now satisfied that the angles on the two sides of the basal plane  $c$  are intended to be truly equal, a supposition which is still further strengthened by the near equality of the values on each side of  $c$  in the first of these three zones; the other two zones each exhibited a second  $q$ -face, but it was too minute to give trustworthy readings.

We have now completed the measurement of the zones indicated on



the projection by the primitive circle and the diameters, and should next consider those indicated on the projection by the circular arcs terminating at parallel  $m$  and  $n$  poles. There are three such arcs on each side of the  $mcm$  diameters, symmetrical to the latter, and four symmetrically on each side of the  $ncn$  diameters; each arc-zone occurs thus in duplicate on the two sides of a diameter, and as there are three similar diameters  $mcm$  or  $ncn$  the same zone occurs six times altogether, and there are consequently seven different arc-zones repeated thus six times each. In every case the zones are only half-zones, or  $180^\circ$  zones, like the diametral zones, as the crystal is only singly terminated, but if it had been doubly terminated they would have been complete  $360^\circ$  zones. Many of the angles are repeated twice in each semi-zone, that is, they occur once in each quadrant, hence it is possible that twelve independent values of the same angle may be obtained from this single crystal, derived from absolutely different faces, symmetrically situated.

In the measurement of these arc-zones, or cross-zones as they are sometimes called, much labour in resetting the crystal may be saved if those about each diameter are measured while the crystal is set for the measurement of the diametral zone itself. It is then only necessary that the adjustment for the latter zone shall be done fairly approximately by the hand-setting on the wax, that is, so that the crystal is approximately adjusted for the diametral zone when the adjusting movements are all in their normal zero positions; only a little use of them is required then for the fine adjustment of that zone, and practically the whole of the circular movement of each of the two adjusting segments is available for the adjustment of the arc-zones about that diameter, without any resetting of the crystal on the wax. After a little experience in goniometrical measurement the importance of this point will be realised, both as regards the saving of trouble and the chance, ever present during hand-movement of the crystal on the wax, of losing, by its becoming detached, a valuable and possibly half-measured minute crystal. For this reason it is advisable to construct at once the stereographic projection of the first zones tackled, in this case say the primitive zone and a couple of diametral zones, an  $m$  and an  $n$  zone; so that it is possible after tentatively also drawing in the projections of the other similar diametral zones, to see early on in the work what arc-zones there are which ought to be measured, and then their measurement can be carried out as recommended, while each diametral zone in turn is *in situ* on the wax, so that none but the first will have to be reset. The mode of finding any facial pole on the projection has been fully described in Chapter VI. In the case of a pole on a diametral zone, the procedure is very simple. For instance, to find the pole of the face  $o=(10\bar{1}1)$  on the diameter  $mcm$ , we mark off from  $m=(10\bar{1}0)$  along the primitive circle on either side, say towards  $m=(01\bar{1}0)$ , an arc equal to the measured angle  $mo=(10\bar{1}0):(10\bar{1}1)$  which was found to be  $49^\circ 42'$ , and we join the point thus marked off to the opposite pole of the diametral zone, which is identical with the pole  $n=(1\bar{2}10)$ . The point of intersection of this line and the diameter  $mcm$  is the position of the pole  $o=(10\bar{1}1)$ . The same distance  $co$  can then be marked off along the other five radii  $mc$  in order to get the positions of the other  $o$  poles. A similar procedure is then followed with regard to the other poles on these  $mcm$  diameters, and for those on the  $ncn$  diameters. The various arc-zones can then be readily drawn in with the compasses, to pass through the ends of the diameters and the various poles on the zones, the proper radius being found in each case by the ordinary method of elementary geometry, of constructing a circular arc to pass through three given points; in every case the centre of the arc will lie on a diameter, so that the radius can even be found by trial.

In the next tables are given the results of the measurements of the seven arc-zones which have been referred to. In only two cases where twelve independent values are possible did the whole of the twelve different faces yield good images; all doubtful cases have been ignored and do not appear in the tables, so that the angular values which do appear are either derived from "A" faces, or from such as left no doubt as to the trustworthiness of their signal images. From the very close equality of the values in each quadrant, or occurring in positions which should be symmetrical if the crystal be truly hexagonal, there can be no further doubt as to this latter being a real fact. Hence, the mean of like angles may with safety be taken, for in no case are all the angles in a zone equal, as was the case with the prism zone, where all were 30°. The well-nigh absolute identity of individual "A" values of symmetrically placed angles in each one and the same zone is, however, as cannot be too strongly or too frequently emphasised, the only real goniometrical test or proof of that symmetry.

### 3 ARC-ZONES IN DUPLICATE ABOUT A DIAMETER *mcm*.

Readings.	Angles.	Readings.	Angles.
$\left\{ \begin{array}{l} m \ 360^\circ \ 0' A \\ o'' \ 281 \ 17 \\ o'' \ 258 \ 41 A \\ m \ 179 \ 59 A \end{array} \right.$	$\left\{ \begin{array}{l} mo'' \ 78^\circ \ 43' \\ o''o'' \ 22 \ 36 \\ o''m \ 78 \ 42 A \end{array} \right.$	$\left\{ \begin{array}{l} m \ 180^\circ \ 0' A \\ o'' \ 101 \ 16 \\ o'' \ 78 \ 49 \\ m \ 0 \ 0 A \end{array} \right.$	$\left\{ \begin{array}{l} mo'' \ 78^\circ \ 44' \\ o''o'' \ 22 \ 27 \\ o''m \ 78 \ 49 \end{array} \right.$
$\left\{ \begin{array}{l} m \ 360 \ 0 A \\ q \ 315 \ 42 A \\ o \ 288 \ 52 A \\ o \ 251 \ 6 A \\ q \ 224 \ 15 A \\ m \ 179 \ 58 A \end{array} \right.$	$\left\{ \begin{array}{l} mq \ 44 \ 18 A \\ qo \ 26 \ 50 A \\ oo \ 37 \ 46 A \\ oq \ 26 \ 51 A \\ qm \ 44 \ 17 A \end{array} \right.$	$\left\{ \begin{array}{l} m \ 360 \ 0 A \\ q \ 315 \ 42 \\ o \ 288 \ 50 A \\ o \ 251 \ 5 A \\ q \ 224 \ 14 A \\ m \ 180 \ 0 A \end{array} \right.$	$\left\{ \begin{array}{l} mq \ 44 \ 18 \\ qo \ 26 \ 52 \\ oo \ 37 \ 45 A \\ oq \ 26 \ 51 A \\ qm \ 44 \ 14 A \end{array} \right.$
	$mo \ 71^\circ \ 8' A$ $om \ 71 \ 8 A$		$mo \ 71^\circ \ 10' A$ $om \ 71 \ 5 A$
$\left\{ \begin{array}{l} m \ 360 \ 0 A \\ o' \ 295 \ 27 A \\ q \ 269 \ 57 A \\ o' \ 244 \ 26 A \\ m \ 180 \ 0 A \end{array} \right.$	$\left\{ \begin{array}{l} mo' \ 64 \ 33 A \\ o'q \ 25 \ 30 A \\ qo' \ 25 \ 31 A \\ o'm \ 64 \ 26 A \end{array} \right.$	$\left\{ \begin{array}{l} m \ 180 \ 0 A \\ o' \ 115 \ 32 A \\ q \ 90 \ 1 A \\ o' \ 64 \ 29 A \\ m \ 0 \ 1 A \end{array} \right.$	$\left\{ \begin{array}{l} mo' \ 64 \ 28 A \\ o'q \ 25 \ 31 A \\ qo' \ 25 \ 32 A \\ o'm \ 64 \ 28 A \end{array} \right.$

A similar series of measurements were also made for the six analogous arc-zones about each of the other two *mcm* diameters, and as no advantage would be gained by transcribing the contents of the note-book for these precisely similar measurements, we can at once collect together the various values obtained for like angles, including those derived from the other two sets of zones as well as those set down above.

The mean values derived were :

$mo'' = 78^\circ \ 45'$ , and  $o''o'' = 22^\circ \ 32'$ ;  $mq = 44^\circ \ 16'$ ,  $qo = 26^\circ \ 51'$ ,  $mo = 71^\circ \ 9'$ , and  $oo = 37^\circ \ 45'$ ;  $mo' = 64^\circ \ 29'$ , and  $o'q = 25^\circ \ 31'$ .

In a similar manner, the results of the measurements of one of the three sets of four zones in duplicate about an *ncn* diameter will next be given. The individual values of analogous angles were collected together, the similar values for the two other sets added to them, and the mean extracted for each angle.

4 ARC-ZONES IN DUPLICATE ABOUT A DIAMETER *ncn*.

Readings.	Angles.	Readings.	Angles.
$\left\{ \begin{array}{l} n \ 180^\circ \ 0' A \\ o'' \ 109 \ 46 A \\ o'' \ 70 \ 15 A \\ n \ 0 \ 1 A \end{array} \right.$	$\left. \begin{array}{l} no'' \ 70^\circ \ 14' A \\ o''o'' \ 39 \ 31 A \\ o''n \ 70 \ 14 A \end{array} \right\}$	$\left\{ \begin{array}{l} n \ 70^\circ \ 13' \\ o'' \ 0 \ 0 A \end{array} \right.$	$no'' \ 70^\circ \ 13'$
$\left\{ \begin{array}{l} n \ 360 \ 12 A \\ o \ 304 \ 18 A \\ o'' \ 270 \ 12 A \\ o \ 236 \ 8 \\ n \ 180 \ 7 \end{array} \right.$	$\left. \begin{array}{l} no \ 55 \ 54 A \\ oo'' \ 34 \ 6 A \\ o''o \ 34 \ 4 \\ on \ 56 \ 1 \end{array} \right\}$	$\left\{ \begin{array}{l} n \ 360 \ 0 A \\ o \ 304 \ 5 A \\ o'' \ 270 \ 0 \end{array} \right.$	$\left. \begin{array}{l} no \ 55 \ 54 A \\ oo'' \ 34 \ 5 \end{array} \right\}$
$\left\{ \begin{array}{l} n \ 360 \ 0 A \\ o' \ 318 \ 15 A \\ o \ 269 \ 59 A \\ o' \ 221 \ 45 A \\ n \ 180 \ 1 A \end{array} \right.$	$\left. \begin{array}{l} no' \ 41 \ 45 A \\ o'o \ 48 \ 16 A \\ oo' \ 48 \ 14 A \\ o'n \ 41 \ 44 \end{array} \right\}$	$\left\{ \begin{array}{l} n \ 360 \ 0 A \\ o' \ 318 \ 15 A \\ o' \ 221 \ 45 A \\ n \ 180 \ 1 \end{array} \right.$	$\left. \begin{array}{l} no' \ 41 \ 45 A \\ o'o' \ 96 \ 30 A \\ o'n \ 41 \ 44 \end{array} \right\}$
$\left\{ \begin{array}{l} n \ 180 \ 0 A \\ q \ 114 \ 24 A \\ q \ 65 \ 35 A \\ n \ 0 \ 1 A \end{array} \right.$	$\left. \begin{array}{l} nq \ 65 \ 36 A \\ qq \ 48 \ 49 A \\ qn \ 65 \ 34 A \end{array} \right\}$	$\left\{ \begin{array}{l} n \ 180 \ 0 \\ q \ 114 \ 25 A \\ q \ 65 \ 34 A \\ n \ 0 \ 0 \end{array} \right.$	$\left. \begin{array}{l} nq \ 65 \ 35 \\ qq \ 48 \ 51 A \\ qn \ 65 \ 34 \end{array} \right\}$

The mean values for these angles in the four arc-zones are :

$no'' = 70^\circ 15'$ , and  $o''o'' = 39^\circ 31'$ ;  $no = 55^\circ 56'$ , and  $oo'' = 34^\circ 4'$ ;  $no' = 41^\circ 44'$ , and  $o'o = 48^\circ 15'$ ;  $nq = 65^\circ 34'$ , and  $qq = 48^\circ 51'$ .

This completes the goniometrical work in connection with apatite, all the numerous zones on the crystal having now been measured, in all 49 zones, namely, the primitive-circle prism zone, six diametral zones, and 42 arc-zones, the diametral zones being of two different kinds and the arc-zones of seven different kinds. Hence, we have only to consider, as zones composed of different angles, (1) the prism zone, (2) two diametral zones, and (3) seven arc-zones, the rest being repetitions of these in accordance with the symmetry. The values of the angles in these 10 zones will be found tabulated at the conclusion of this chapter, after the necessary calculations of angles and elements have been made.

**Calculation of angles and elements.** Basal angle,  $co = (0001) : (10\bar{1}1) = 40^\circ 18'$ .

It is convenient to proceed first to find the position of the pole  $o'$  on the same radius *moc*.

To find  $mo' = (10\bar{1}0) : (20\bar{2}1)$ .

The pole  $o'$  may be considered the fourth pole in the  $90^\circ$  zone [*moc*], and the anharmonic ratio of four poles in a zone employed. The conditions are represented by the diagram in Fig. 265, from which we at once deduce, as explained in Chapter VI., that :

$$\frac{10\bar{1}0 \ 0001}{20\bar{2}1 \ 10\bar{1}1} \cdot \frac{10\bar{1}1}{0001} = \frac{\sin mo'}{\sin 49^\circ 42'} \cdot \frac{\sin 40^\circ 18'}{\sin co'}$$

$$\frac{10\bar{1}1 \ 20\bar{2}1}{10\bar{1}0 \ 0001} = \frac{\sin co'}{\sin mo'}$$

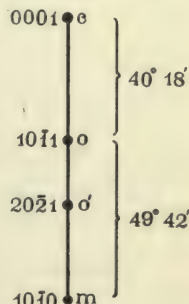


FIG. 265.



$$\frac{1}{1} \cdot \frac{1}{2} = \frac{\sin mo'}{\cos mo'} \cdot \frac{\sin 40^\circ 18'}{\cos 40^\circ 18'} = \tan mo' \cdot \tan 40^\circ 18'$$

$$\tan mo' = \frac{1}{2} \cot 40^\circ 18'. \quad mo' = 30^\circ 31'.$$

This value is identical with the mean measured angle, five individual "A" values of which only varied one minute on either side of it.

We can then get  $oo'$  by the difference of this angle and  $mo$ , thus :

$$oo' = 49^\circ 42' - 30^\circ 31' = 19^\circ 11'.$$

This is again identical with the mean measured value.

We may next proceed conveniently to find  $nq = (11\bar{2}0) : (11\bar{2}1)$  and  $qo' = (11\bar{2}1) : (20\bar{2}1)$ .

This we may do from the right-angled triangle  $co'q$ ,  $(0001) : (20\bar{2}1) : (11\bar{2}1)$ , in which we know the side  $co'$  ( $40^\circ 18' + 19^\circ 11' = 59^\circ 29'$ ), the angle at  $c$  ( $30^\circ$ ), and the right angle at  $q$ , and also that  $cq$  is the complement of  $nq$ . From the Napierian diagram (Fig. 53, page 107) we derive :

$$\sin o'q = \sin 30^\circ \sin 59^\circ 29'; \quad \sin cq = \cot 30^\circ \tan o'q.$$

$$o'q = 25^\circ 31'. \quad cq = 55^\circ 45'.$$

$$\text{Then} \quad nq = (11\bar{2}0) : (11\bar{2}1) = 90^\circ - 55^\circ 45' = 34^\circ 15'.$$

$$\text{Also} \quad o'm = (20\bar{2}1) : (1\bar{1}00) = 90^\circ - 25^\circ 31' = 64^\circ 29'.$$

These four values are all absolutely identical with the mean measured values, the whole of the individual values having also been remarkably close, showing the extraordinary accuracy with which, in a good crystal, the intention of nature is carried out.

We may next address ourselves to the calculation of  $mq = (10\bar{1}0) : (11\bar{2}1)$ . We can again use a right-angled triangle, namely,  $mqn$   $(10\bar{1}0) : (11\bar{2}1) : (11\bar{2}0)$ , in which the right angle is at  $n$ , the side  $mn$  is  $30^\circ$ , and the side  $nq$  we have just found to be  $34^\circ 15'$ . Setting out the usual Napierian diagram, we at once deduce from it :

$$\cos mq = \cos 30^\circ \cos 34^\circ 15'. \quad mq = 44^\circ 17'.$$

The mean measured angle was  $44^\circ 16'$ .

Continuing the calculation of the angles in the same zone, we should next find  $qo = (11\bar{2}1) : (01\bar{1}1)$ , and  $oo = (01\bar{1}1) : (1\bar{1}01)$ .

Commencing with the latter, we can find the half of it from the right-angled triangle  $c = (0001)$ ,  $o = (01\bar{1}1)$ ,  $(1\bar{2}1\bar{2})$ ; the last-named possible face is not developed, but the symbol serves to mark the third corner of the triangle in question, in which we know the side  $co = 40^\circ 18'$ , the basal angle, and the angles at  $c$  and at  $(1\bar{2}1\bar{2})$ , which are  $30^\circ$  and  $90^\circ$  respectively. Making up, therefore, the usual Napierian diagram, we deduce :

$$\sin (\frac{1}{2}oo) = \sin o : (1\bar{2}1\bar{2}) = \sin 30^\circ \sin 40^\circ 18'.$$

$$\frac{1}{2}oo = 18^\circ 52', \text{ and } oo = 37^\circ 44'.$$

$$\text{Then} \quad oq = (01\bar{1}1) : (11\bar{2}1) = 90^\circ - (mq + \frac{1}{2}oo) = 90^\circ - 63^\circ 9' = 26^\circ 51'.$$

$$44^\circ 17' + 18^\circ 52'.$$

Also  $mo = (10\bar{1}0) : (01\bar{1}1) = 44^\circ 17' + 26^\circ 51' = 71^\circ 8'$ , which was also one of the well-measured angles.

The mean measured values of these three angles  $oo$ ,  $oq$ , and  $mo$  in this zone were respectively  $37^\circ 45'$ ,  $26^\circ 51'$ , and  $71^\circ 9'$ , the first and third being thus only one minute removed from, and the second identical with, the calculated value.

In order to complete the calculation of the angles in the diametral zones and those of the arc-zones terminating at  $m$  poles, it remains to find the position of the pole  $o'' = (10\bar{1}2)$  in the zone  $[moc]$ , and the angle  $mo'' = (1\bar{1}00) : (10\bar{1}2)$ .

Commencing with the former, we can find  $co'' = (0001) : (10\bar{1}2)$  from the anharmonic ratio of the four poles  $c$ ,  $o''$ ,  $o$ ,  $m$ , the conditions being defined diagrammatically in Fig. 266. The ratio is as follows :

$$\begin{array}{l}
 10\bar{1}0 \quad 0001 \\
 \times \qquad \times \\
 10\bar{1}1 \quad 10\bar{1}2 = \frac{\sin 49^\circ 42'}{\sin mo''} \cdot \frac{\sin co''}{\sin 40^\circ 18'} \\
 10\bar{1}0 \cdot 0001 \\
 \times \qquad \times \\
 10\bar{1}2 \quad 10\bar{1}1 \\
 \frac{1}{2} \cdot \frac{1}{1} = \frac{1}{2} = \frac{\sin co''}{\cos co''} \cdot \frac{\cos 40^\circ 18'}{\sin 40^\circ 18'}
 \end{array}$$

$$\tan co'' = \frac{1}{2} \tan 40^\circ 18'. \quad co'' = 22^\circ 59'.$$

$$\text{Then } oo'' = co - co'' = 40^\circ 18' - 22^\circ 59' = 17^\circ 19'.$$

The former value is identical with the measured value, and the latter is only 1' removed.

To find  $mo'' = (1\bar{1}00) : (10\bar{1}2)$ .

We can readily find first the complement of  $mo''$  from the right-angled triangle  $c = (0001) : o'' = (10\bar{1}2) : (11\bar{2}4)$ , the last pole being that of a possible but not of an actually developed face in the zone  $[cq n]$ , the symbol of which, however, serves to mark that corner of the triangle at which the right angle occurs. We know that the angle at  $c$  is  $30^\circ$ , and have just found the side  $co''$  to be  $22^\circ 59'$ . From the Napierian diagram expressing the conditions we deduce :

$$\sin o'' : (11\bar{2}4) = \sin 30^\circ \sin 22^\circ 59'. \quad o'' : (11\bar{2}4) = 11^\circ 15'.$$

$$\text{Hence } o''o'' = 22^\circ 30', \text{ and } mo'' = 90^\circ - 11^\circ 15' = 78^\circ 45'.$$

The mean measured value of  $mo''$  was identical with this value, namely,  $78^\circ 45'$ , and that of  $o''o''$  was  $22^\circ 32'$ , only two minutes removed from the calculated value.

We may now proceed to calculate the values of the angles in the arc-zones ending at  $n$ -poles.

To find  $no = (\bar{1}2\bar{1}0) : (01\bar{1}1)$  and  $oo'' = (01\bar{1}1) : (10\bar{1}2)$ .

We can readily find the latter from the right-angled triangle  $co''o$ , the particular  $o''$  and  $o$  poles being those having the indices just stated. In this triangle the right angle is at  $o'' = (10\bar{1}2)$ , the angle at  $c = (0001)$  is  $60^\circ$ , the side  $co'' = (0001) : (10\bar{1}2)$  is  $22^\circ 59'$ , and the side  $co = (0001) : (01\bar{1}1)$  is  $40^\circ 18'$ . Making the usual diagram we obtain :

$$\sin o''o = \sin 60^\circ \sin 40^\circ 18'. \quad o''o = 34^\circ 4'.$$

$$\text{Then } no = 90^\circ - 34^\circ 4' = 55^\circ 56'.$$

Both these calculated values are identical with the mean measured values.

Taking now the next arc  $n, o', o$ , or its analogue ending at the axis  $-A_3$ , we can find  $no' = (11\bar{2}0) : (20\bar{2}1)$  from the triangle  $m = (10\bar{1}0) : n = (11\bar{2}0) : o' = (20\bar{2}1)$ , in which the angle at  $m$  is a right angle, the side  $mn$  is  $30^\circ$ , and the side  $mo'$  is  $30^\circ 31'$ . From the diagram and Napier's rules we derive :

$$\cos no' = \cos 30^\circ \cos 30^\circ 31'. \quad no' = 41^\circ 45'.$$

$$\text{Then } o'o = (20\bar{2}1) : (1\bar{1}01) = 90^\circ - 41^\circ 45' = 48^\circ 15'.$$

The latter is identical with the mean measured value, while that for  $no'$  was only 1' removed, namely,  $41^\circ 44'$ .

Taking now the next and most outward arc-zone terminating at  $n$  on the projection, to find  $nq = (\bar{1}2\bar{1}0) : (11\bar{2}1)$ .

This angle can readily be found from the triangle  $n = (\bar{1}2\bar{1}0) : q = (11\bar{2}1) : n = (11\bar{2}0)$ , in which the angle at  $n = (11\bar{2}0)$  is a right angle,  $nn$  is  $60^\circ$ , and  $n = (11\bar{2}0) : q$  is  $34^\circ 15'$ . From the Napierian diagram we get :

$$\cos nq = \cos 60^\circ \cos 34^\circ 15'. \quad nq = 65^\circ 35'.$$

$$\text{Then also } qq = (11\bar{2}1) : (2\bar{1}\bar{1}1) = 2(90^\circ - 65^\circ 35') = 48^\circ 50'.$$

The mean measured angles were  $nq = 65^\circ 34'$  and  $qq = 48^\circ 51'$ , in each case only one minute removed from the calculated value.

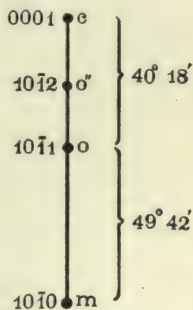


FIG. 266.

There is still the innermost of these  $n$ -arc-zones remaining, in which we have to calculate  $no'' = (\bar{1}2\bar{1}0) : (01\bar{1}2)$ .

We can obtain the complement of this angle most conveniently, namely, half  $o''o'' = (01\bar{1}2) : (\bar{1}102)$ , for this angle forms one side of the triangle  $c = (0001) : o'' = (01\bar{1}2) : (10\bar{1}4)$ , the last pole being that one on the diametral zone  $[moc]$  which marks the half of  $o''o''$ , and, while not being that of a developed face, is useful to insert in the projection for the purpose of marking the third corner of the triangle under consideration. In this triangle the angle at  $(10\bar{1}4)$  is a right angle, the side  $co''$  we have found to be  $22^\circ 59'$ , and the angle at  $c$  is  $60^\circ$ . Constructing our diagram we have, by Napier's rules,

$$\sin(10\bar{1}4) : o'' = \sin 60^\circ \sin 22^\circ 59'. \quad (10\bar{1}4) : o'' = 19^\circ 46'.$$

From which we get  $no'' = 90^\circ - 19^\circ 46' = 70^\circ 14'$ ,

and  $o''o'' = 2(19^\circ 46') = 39^\circ 32'$ .

The mean measured value of  $no''$  was  $70^\circ 15'$ , and of  $o''o''$   $39^\circ 31'$ , an agreement within one minute.

This completes the calculations of all the angles between faces actually measurable on the crystal, but it will be interesting to conclude by also calculating the positions of the two class-determining faces also present of the forms  $s = \{21\bar{3}1\}$  and  $p = \{21\bar{3}0\}$ , which were too minute to afford trustworthy measurements.

To find the position of the right pyramid face  $s = (21\bar{3}1)$  in the zone  $[msq]$ , in other words, to find  $ms = (10\bar{1}0) : (21\bar{3}1)$ .

This we can do by making use of the anharmonic ratio of the four poles  $m = (10\bar{1}0)$ ,  $s = (21\bar{3}1)$ ,  $q = (11\bar{2}1)$ , and  $(\bar{1}2\bar{1}2)$  in the  $90^\circ$ -zone ending at the last-mentioned pole on the  $+A_2$  diameter, which is not, however, represented by a developed face on the crystal. The conditions are shown in Fig. 267, from which we deduce:

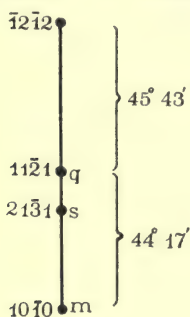


FIG. 267.

$$\begin{array}{r} 10\bar{1}0 \quad \bar{1}2\bar{1}2 \\ \times \quad \times \\ 21\bar{3}1 \quad 11\bar{2}1 \\ \hline 10\bar{1}0 \quad \bar{1}2\bar{1}2 = \frac{\sin ms}{\sin 44^\circ 17'} \cdot \frac{\sin 45^\circ 43'}{\sin (\bar{1}2\bar{1}2) : s} \\ \times \quad \times \\ 11\bar{2}1 \quad 21\bar{3}1 \\ \hline \bar{1} \quad 3 \\ \bar{1} \quad 5 = \frac{\sin ms}{\cos ms} \cdot \frac{\sin 45^\circ 43'}{\cos 45^\circ 43'} \end{array}$$

$$\tan ms = \frac{3}{5} \cot 45^\circ 43'$$

$$ms = 30^\circ 20', \text{ and } sq = 44^\circ 17' - 30^\circ 20' = 13^\circ 57'.$$

Next, to find  $ms = (01\bar{1}0) : (21\bar{3}1)$  in the zone  $[msq]$ .

The zone in question measures  $90^\circ$  from  $m$  to  $q$ , so that the anharmonic ratio can again be employed in its simpler form. The conditions are given in Fig. 268, from which we derive:

$$\begin{array}{r} 01\bar{1}0 \quad 2\bar{1}\bar{1}1 \\ \times \quad \times \\ 21\bar{3}1 \quad 20\bar{2}1 \\ \hline 01\bar{1}0 \quad 2\bar{1}\bar{1}1 = \frac{\sin ms}{\sin 64^\circ 29'} \cdot \frac{\sin 25^\circ 31'}{\sin qs} \\ \times \quad \times \\ 20\bar{2}1 \quad 21\bar{3}1 \\ \hline \bar{2} \quad 2 \\ \bar{2} \quad 4 = \frac{\sin ms}{\cos ms} \cdot \frac{\sin 25^\circ 31'}{\cos 25^\circ 31'} \end{array}$$

$$\tan ms = \frac{1}{2} \cot 25^\circ 31'. \quad ms = 46^\circ 20'.$$

Then  $so' = (21\bar{3}1) : (20\bar{2}1) = 64^\circ 29' - 46^\circ 20' = 18^\circ 9'$

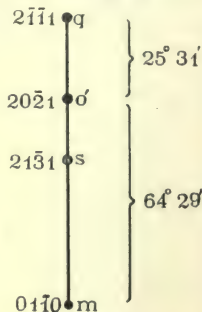


FIG. 268.

We have next to find the position of  $p = (21\bar{3}0)$  in the prism zone, that is, to find  $mp = (10\bar{1}0) : (21\bar{3}0)$ . The conditions are shown in Fig. 269, and we derive therefrom:





form  $\{10\bar{1}0\}$ , say between the faces  $(10\bar{1}1)$  and  $(10\bar{1}0)$ , which has been shown to be  $49^\circ 42'$ . This method will be found developed in detail, with an explanatory illustration on page 370 of Chapter XXIII., in connection with the axial ratio of quartz. From the analysis there given, the combination of the two primary rhombohedra of quartz corresponding exactly to the hexagonal first order pyramid of apatite, it will be clear that :

$$\frac{c}{a} = \frac{\sqrt{3}}{2} \tan [\text{complement of angle } (10\bar{1}1) : (10\bar{1}0)]$$

and this in the case of apatite is :

$$\frac{c}{a} = \frac{\sqrt{3}}{2} \tan 40^\circ 18'.$$

As the angle  $40^\circ 18'$  is the basal angle  $co$ , it is a most appropriate angle to take for the calculation of the elements. On calculating the axial ratio from this simple equation, we find that  $\frac{c}{a} = 0.7345$ .

The results of the two methods of calculation are in such close agreement that we can with confidence take the ratio of the axes to be :

$$a : c = 1 : 0.7345.$$

This result is within one unit in the fourth decimal place of the value derived from the measurements of v. Kokscharow.

It now only remains to collect together the results of the investigation of this crystal of apatite—one of the most perfect little crystals, and (for its minute size) one of the richest in faces, with which the author has ever had the pleasure to work—and to present them in concise tabular form. The agreement between the observed and calculated angles is most satisfactory, the maximum difference being only  $2'$ .

TABLE OF RESULTS FOR CRYSTAL OF APATITE,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ .  
Cl

**Crystal-system :** Hexagonal. **Class :** 25, bipyramidal.

**Ratio of Axes :**  $a : c = 1 : 0.7345$ .

**Forms observed :**  $c = \{0001\}$ ,  $m = \{10\bar{1}0\}$ ,  $n = \{11\bar{2}0\}$ ,  $p = \{21\bar{3}0\}$ ,  
 $o = \{10\bar{1}1\}$ ,  $o' = \{20\bar{2}1\}$ ,  $o'' = \{10\bar{1}2\}$ ,  $q = \{11\bar{2}1\}$ ,  
 $s = \{21\bar{3}1\}$ .

**Interfacial angles:** as given in the following table, the basal angle being marked with an asterisk, and the brackets indicating the zones.

Angle.	No. of Measurements.	Limits.	Mean observed.	Calculated Value.	Difference.
$\left\{ \begin{array}{l} mn = (10\bar{1}0) : (11\bar{2}0) \\ mp = (10\bar{1}0) : (21\bar{3}0) \\ pn = (21\bar{3}0) : (11\bar{2}0) \\ mm = (10\bar{1}0) : (01\bar{1}0) \end{array} \right.$	12 .. .. 6	29° 56'–30° 5' .. .. 59 54–60 5	30° 0' .. .. 60 0	30° 0' 19 6 10 54 60 0	0' .. .. 0
$\left\{ \begin{array}{l} mo' = (10\bar{1}0) : (20\bar{2}1) \\ o'o = (20\bar{2}1) : (10\bar{1}1) \\ oo'' = (10\bar{1}1) : (10\bar{1}2) \\ o''c = (10\bar{1}2) : (0001) \\ oc = (10\bar{1}1) : (0001) \end{array} \right.$	6 6 4 4 6	30 30–30 32 19 9–19 14 17 15–17 24 22 56–23 1 40 15–40 20	30 31 19 11 17 20 22 59 40 18	30 31 19 11 17 19 22 59 *	0 0 1 0 ..
$\left\{ \begin{array}{l} nq = (11\bar{2}0) : (11\bar{2}1) \\ qc = (11\bar{2}1) : (0001) \end{array} \right.$	4 4	34 14–34 17 55 44–55 48	34 15 55 45	34 15 55 45	0 0
$\left\{ \begin{array}{l} mo' = (10\bar{1}0) : (02\bar{2}1) \\ o'q = (02\bar{2}1) : (1\bar{2}11) \\ ms = (01\bar{1}0) : (21\bar{3}1) \\ so' = (21\bar{3}1) : (20\bar{2}1) \end{array} \right.$	12 8 .. ..	64 24–64 33 25 30–25 32 .. ..	64 29 25 31 .. ..	64 29 25 31 46 20 18 9	0 0 .. ..
$\left\{ \begin{array}{l} ms = (10\bar{1}0) : (21\bar{3}1) \\ sq = (21\bar{3}1) : (11\bar{2}1) \\ mq = (10\bar{1}0) : (11\bar{2}1) \\ qo = (11\bar{2}1) : (01\bar{1}1) \\ mo = (10\bar{1}0) : (01\bar{1}1) \\ oo = (01\bar{1}1) : (1101) \end{array} \right.$	.. .. 10 6 7 3	.. .. 44 12–44 18 26 50–26 52 71 5–71 12 37 44–37 46	.. .. 44 16 26 51 71 9 37 45	30 20 13 57 44 17 26 51 71 8 37 44	.. .. 1 0 1 1
$\left\{ \begin{array}{l} mo'' = (10\bar{1}0) : (01\bar{1}2) \\ o''o'' = (01\bar{1}2) : (1102) \end{array} \right.$	5 2	78 42–78 49 22 27–22 36	78 45 22 32	78 45 22 30	0 2
$\left\{ \begin{array}{l} nq = (11\bar{2}0) : (2\bar{1}11) \\ qq = (2\bar{1}11) : (1\bar{2}11) \end{array} \right.$	8 3	65 33–65 36 48 49–48 53	65 34 48 51	65 35 48 50	1 1
$\left\{ \begin{array}{l} no' = (11\bar{2}0) : (20\bar{2}1) \\ o'o = (20\bar{2}1) : (1101) \end{array} \right.$	12 8	41 42–41 46 48 14–48 17	41 44 48 15	41 45 48 15	1 0
$\left\{ \begin{array}{l} no = (11\bar{2}0) : (10\bar{1}1) \\ oo'' = (10\bar{1}1) : (1102) \end{array} \right.$	8 8	55 53–56 1 34 1–34 6	55 56 34 4	55 56 34 4	0 0
$\left\{ \begin{array}{l} no'' = (11\bar{2}0) : (10\bar{1}2) \\ o''o'' = (10\bar{1}2) : (01\bar{1}2) \end{array} \right.$	7 2	70 12–70 18 39 31–39 31	70 15 39 31	70 14 39 32	1 1
$\left\{ \begin{array}{l} cs = (0001) : (21\bar{3}1) \\ sp = (21\bar{3}1) : (21\bar{3}0) \end{array} \right.$	.. ..	.. ..	.. ..	65 59 24 1	.. ..



## CHAPTER XXII

### TRIGONAL SYSTEM

**Three equal crystallographic axes equally inclined at an angle generally other than  $90^\circ$ .**

**Characterised by a trigonal axis of symmetry.**

THE classes which are here included in a separate trigonal system were formerly considered as hemihedral and tetartohedral classes of the hexagonal system. Although the idea of hemihedrism and tetartohedrism has now been displaced by the consideration of the various classes of crystals as distinct types of homogeneous structures, there is still considerable ground for considering the hexagonal and trigonal classes together; but on the whole, especially as when combined they are no less than twelve in number, it is undoubtedly better to consider the five clearly hexagonal classes as a separate hexagonal system, as was done in the

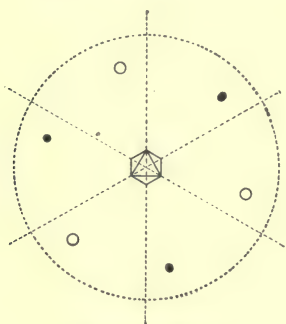


FIG. 271.—Class 17.

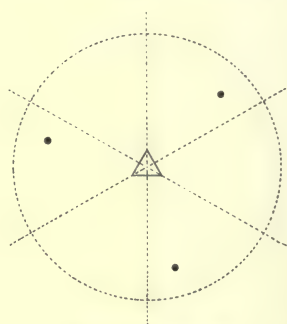


FIG. 272.—Class 16.

last chapter but one, and the seven classes distinguished by the presence of a merely trigonal and not hexagonal axis of symmetry as a separate trigonal system. An interesting link between the two is afforded, however, by class 17 of the trigonal system, in which we have a trigonal axis which is also a hexagonal axis of compound, alternating, or mirror-image symmetry. This case has already been considered in discussing the three instances of compound symmetry, on page 135 in Chapter IX. Fig. 78 representing it in stereographic projection is repeated here in Fig. 271, for the sake of comparison with the purely trigonal axis displayed by class 16 of the trigonal system, the projection of which is given

alongside in Fig. 272. The difference between the two classes is that the purely trigonal axis only necessitates the presence of three faces, those of a trigonal pyramid of the third order in the most general case shown in Fig. 272, the poles of which lie on the same (upper) hemisphere, whereas on the other hand the hexagonal axis of compound symmetry furnishes three additional poles on the other (lower) hemisphere in alternate  $60^\circ$  positions from the first three, by rotation of the latter for  $60^\circ$  round the axis and then immediate reflection across the equatorial plane.

The same system of four crystallographic axes, a principal vertical axis and three axes mutually inclined at  $60^\circ$  in the equatorial plane perpendicular to the principal axis, may be employed with trigonal crystals as for hexagonal crystals. But there is another possible mode of description of purely trigonal crystals which is not only equally suitable, but which is also more in consonance with their structure. Moreover, it avoids the necessity for the use of a fourth axis, enabling us to return to the general Millerian system of three axes. It is consequently known as Miller's method of description, the four-axial method, as pointed out in Chapter XX., being generally referred to as the Bravais-Miller method. The Millerian axes are derived in the following manner.

In the stereographic projection of the general form of the simplest trigonal class, 16, given in Fig. 272, each of the three pyramidal poles lies within one of the  $60^\circ$ -triangles, alternate triangles being left unoccupied, and the trigonal pyramid produced is therefore one of the third order on the analogy of the tetragonal system. But if the special case be considered in which the poles lie on three of the  $60^\circ$ -radii, as shown in Fig. 273, a trigonal pyramid of the first order is produced, employing the nomenclature of the hexagonal system. But three of the  $60^\circ$ -radii only are occupied by the poles, namely, those marked with a positive sign in Fig. 273; the other three radii marked with a negative sign, however, are the projections of the edges of the pyramid, for these latter lie in the planes formed by the vertical trigonal axis with each of the three diameters representing in the projection the result of the operation of that axis. In Miller's system

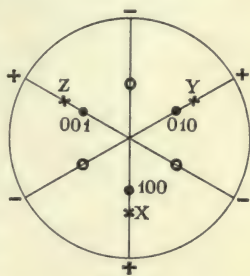


FIG. 273.

of axes **these three edges of the primary first order trigonal pyramid are taken as the three axial directions.** They are equal and equally inclined to each other, but the angle is not  $90^\circ$ , except in a special case which is crystallographically possible. The actual edges themselves, as represented by the three negative radii, are considered as the negative halves of the axes, and their prolongations upwards, beyond the point of their intersection (the apex of the pyramid), are taken as the positive halves. **The three faces of the pyramid, the poles of which fall on the positive halves, are the axial planes, and, just as in the case of the cube, the faces of which are the crystallographic axial planes of the cubic**

system, they have symbols containing the same index numbers, namely, (100), (010), and (001). The trigonal solid formed by the three pyramidal faces thus chosen as axial planes, and their three parallel fellow-faces at the other side of the centre, is the rhombohedron. Its projection is obtained by placing rings on the negative radii at the same distance from the centre as the three solid-dot poles. It may be regarded as a cube more or less deformed by compression along a diagonal, the edges remaining the same and equal but the angles being deformed out of their  $90^\circ$  magnitudes. The cube can thus be legitimately taken as an illustration of the rhombohedron, and as a matter of fact the cube is a special case, crystallographically possible, of the rhombohedron. When a cube is thus set up on one of its solid angles, with a diagonal vertical, representing the trigonal axis, and is compressed along this axis, we have a very fair representation of the rhombohedron and of the Millerian axes (its edges) and axial planes (its faces). If several such rhombohedra of different diagonal dimensions are developed on a crystal, as frequently happens, that one which most nearly resembles a cube is chosen as the primary one, determining the axes, unless the cleavage directions correspond to another rhombohedron, when that would be chosen in preference, as being the most important structurally.

The trigonal (often called rhombohedral) Millerian axial system thus consists of three equal crystallographic axes intersecting at equal angles which are in general other than  $90^\circ$ , and disposed symmetrically about an axis of trigonal symmetry, which is arranged vertically just as is the hexagonal axis of the hexagonal system or the tetragonal axis of the tetragonal system, but which is not in Millerian trigonal notation a crystallographic axis, although it is so when the Bravais-Miller method is used. The stereographic projection of the poles of the axes is shown by the crosses in Fig. 273; they differ from those of the cubic system

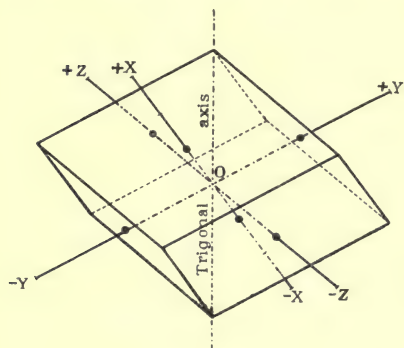


FIG. 274.

by not being identical in position with those of the axial facial-planes (100), (010), and (001). They are also given later in Fig. 292 (page 341), and their exact position is defined in connection with that figure.

The rhombohedron with its three crystallographic axes and the vertical trigonal symmetry axis are shown in Fig. 274. The parametral plane, defining the relative lengths of the axes, is the basal plane, which thus has the symbol (111) in Millerian trigonal notation. This plane is parallel to the equatorial

plane and perpendicular to the trigonal axis, just as it is in the hexagonal system.

The elements in rhombohedral Millerian notation are consequently :

$$a : a : a = 1 : 1 : 1. \quad \alpha = \beta = \gamma = \text{an angle usually other than } 90^\circ.$$



The value of this angle  $\alpha$  is at once obtained by calculation from the goniometrical angle over any of the axial edges, that is, between any pair of rhombohedral faces intersecting in one of the edges chosen as an axial direction (see pages 369 and 378).

The three lower pyramidal faces of the rhombohedron, parallel to the upper three, have the Millerian symbols  $(\bar{1}00)$ ,  $(0\bar{1}0)$ , and  $(00\bar{1})$  respectively, as in the cases of the three faces of the cube parallel to the three chosen as axial planes. Indeed, in general in the trigonal system with Millerian axes, a parallel face has the same indices in the same order, but with all the signs reversed.

This Millerian system of axes is peculiarly suitable for the description of trigonal forms on account of the fact that the space-lattice systems of three of the classes included in the trigonal system are rhombohedral, that is, the elementary parallelepipedon is a rhombohedron. These classes are 17, 20 and 21. The other four classes have the simple trigonal prism for their elementary parallelepipedon, and in no class is the hexagonal prism the fundamental form. Hence there are very good structural grounds for the adoption of the Millerian axes for trigonal forms, and for the consideration of the trigonal as a separate system of symmetry.

The simple trigonal prism just referred to has its poles at the ends of the positive radii (see the more complete trigonal stereographic projection in Fig. 292), its faces being parallel to the trigonal vertical axis. It will be obvious that its facial indices must be  $(2\bar{1}\bar{1})$ ,  $(\bar{1}2\bar{1})$ , and  $(\bar{1}\bar{1}2)$ , for each of the three faces, if imagined to be moved parallel to itself until it touches the ends of the two radii (projections of the axes)  $60^\circ$  on each side of it, will then bisect the radius at the end of which its pole lies, so that the intercept on that axis will be halved and the corresponding index number doubled relatively to the other two. This is the trigonal prism of the first order, which thus always has two of its index numbers equal and of the same sign.

The second order trigonal prism is indicated by the three poles on the primitive circle (Fig. 292) midway between the positive and negative radii; the indices will obviously be  $(10\bar{1})$ ,  $(\bar{1}10)$ , and  $(0\bar{1}1)$ , for the symbol of each face must contain one 0 to indicate the parallelism of the face to one of the three axes, and the two other index numbers must be equal and of opposite sign, to indicate the fact that the pole lies midway between two axial radii of opposite sign, and they can consequently be expressed by a 1 and a  $\bar{1}$ .

Besides the rhombohedron of which the poles are given in Fig. 273, and which is shown in Fig. 274, it must be apparent that there is a second complementary one possible, the poles of which would be obtained by replacing the three dots representing the upper faces  $(100)$ ,  $(010)$ , and  $(001)$  by rings, and the three rings representing the lower faces by dots. The two rhombohedra thus complementary to each other make up together the hexagonal bipyramid of the first order, hence the rhombohedron may be considered as a hemihedral form of the hexagonal system, and was entirely so considered until the development of the theory of crystals as homogeneous structures. The indices of the three faces of the second

rhombohedron in the upper hemisphere are  $(2\bar{1}2)$  for the left face,  $(22\bar{1})$  for the right face, and  $(\bar{1}22)$  for the back face, the form symbol being  $\{122\}$  (see Fig. 292). The fact, however, that the two complementary forms composing together the hexagonal bipyramid thus possess altogether different indices on Miller's system, and that the whole bipyramid, as a form, would therefore have to bear two symbols if Miller's indices were used to describe fully hexagonal forms, is an unanswerable argument against employing Miller's system for such purely hexagonal forms. The Bravais-Miller four-axes system, which describes the whole form by a single symbol, is consequently the only satisfactory one which can be employed with hexagonal forms, and it was for this reason that the four-axes method was employed exclusively in Chapter XX. on the hexagonal system. Miller's axes are, however, perfect for the description of rhombohedral and other trigonal crystals, and, as we have seen, bear a definite relationship to their structure.

The first or primary rhombohedron  $\{100\}$  is generally spoken of as the "direct" or positive one, and the secondary rhombohedron  $\{\bar{1}22\}$  as the "inverse" or negative one. The two forms, and indeed any two trigonal direct and inverse forms in general, are connected by three important and most useful equations. If  $\{pqr\}$  be the indices of the direct or positive form, and  $\{p'q'r'\}$  represent those of the inverse or negative form (the letters  $hkl$  being reserved for use in the Bravais-Miller symbol  $\{hkl\}$ ), then:  $p' = -p + 2q + 2r$ ;  $q' = 2p - q + 2r$ ;  $r' = 2p + 2q - r$ . The particular face the indices of which are afforded by the equations, and which are taken for the form symbol, is that represented by the pole lying on the same diameter in the projection, at an equal distance on the other side of the centre of the primitive circle, and on the same hemisphere as the pole represented by the symbol  $\{pqr\}$ .

We may now proceed to the discussion of the seven classes of the trigonal system. In the list of forms belonging to each class both Bravais-Miller and Millerian indices will be given, as both methods of description are in current use.

The seven classes of the trigonal system may be derived successively from class 16, the primitive class of the system possessing only the essential trigonal axis of symmetry, the projection of which is shown in Fig. 272. The general form of that class has been shown to be an upper or a lower trigonal (three-faced) pyramid, the poles of the upper one being exhibited in the figure.

Three of the other classes are obtained by adding to this upper pyramid three other similar lower faces in three different ways, to produce a simple closed form of higher symmetry. These three modes are indicated by Figs. 271 (given at the beginning of this chapter), 275, and 276. It is as if the lower pyramid were rotated round the vertical axis, with respect to the upper pyramid, and arrested in its rotation at three different positions.

In class 17 (Fig. 271) the poles (rings) appear in the projection equally removed, at  $60^\circ$ , from the three upper ones. This is the case already alluded to which occurs when the trigonal axis acts also as a hexagonal axis of compound or reflective symmetry. The general

form shown in the projection is a rhombohedron of the third order, which gives its name to the class. In class 18 (Fig. 275) the poles are at unequal distances between those of the upper poles, but analogously disposed as regards the crystallographic axes, so that they are represented by equal indices. These conditions are fulfilled when there are

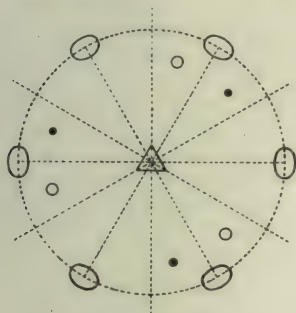


FIG. 275.—Class 18.

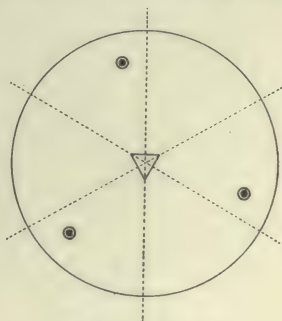


FIG. 276.—Class 19.

three digonal axes parallel to the basal plane, which are shown as diameters in the projection, intermediate between those representing the Millerian and identical with the Bravais-Millerian crystallographic axes. The trigonal bipyramid thus produced is of trapezohedral character. It is to this class 18 that quartz belongs. In class 19 (Fig. 276) the lower trigonal pyramid is precisely underneath the upper one, the poles being represented by rings around the dots. This obviously occurs when the basal plane is a plane of symmetry. The solid produced is the ordinary trigonal bipyramid.

A further class, 20, is derived directly from class 16 by the introduction of a symmetry plane parallel to the trigonal axis, and this involves, from the very nature of that axis, two others, making three planes of symmetry inclined at  $120^\circ$  to each other and all parallel to and intersecting in the trigonal axis. They are represented by the three diameters in the projection given in Fig. 277. The resulting solid is a ditrigonal pyramid.

Lastly, we obtain two more classes of higher symmetry by adding to the symmetry elements of class 20 three digonal axes in two different ways. In class 21 the three digonal axes are the same as in class 18, namely, they bisect the angles between the projections of the Millerian crystallographic axes and thus also those between the three symmetry planes containing them. They are consequently identical in direction with the Bravais-Miller horizontal axes. This arrangement gives six lower faces with poles corresponding to the six upper ones

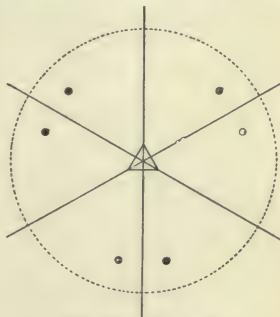


FIG. 277.—Class 20.



but at the alternate  $60^\circ$  positions, as shown in Fig. 278. It is like class 17, only with double poles, one symmetrically on each side of the Millerian crystallographic axes, rendering the solid a ditrigonal instead of merely a trigonal one. It is equivalent to considering the basal plane as a plane of compound (reflective) symmetry, combined with the

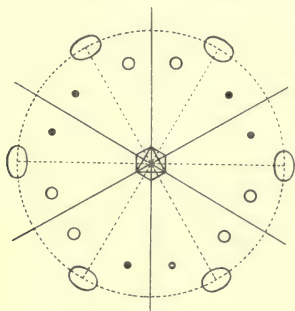


FIG. 278.—Class 21.

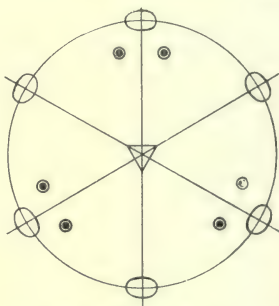


FIG. 279.—Class 22.

operation of a hexagonal axis instead of a trigonal one. The solid produced is the ditrigonal scalenohedron, which is thus of dihexagonal alternating type. This is the important class to which calcite belongs.

Class 22, the class of highest trigonal symmetry, is produced when the three digonal axes are parallel to the three symmetry planes, as shown in Fig. 279. The six lower poles then come immediately underneath the six upper ones, thus rendering the solid, the ditrigonal bipyramid, also symmetrical to the basal plane.

It will be obvious that of the foregoing seven classes of trigonal symmetry only classes 16 and 20 will exhibit hemimorphism, that is, polarity of the two ends of the trigonal axis, while classes 16 and 18 are the only two which afford enantiomorphous pairs of solids, not convertible one into the other by rotation.

Class 19, the trigonal bipyramidal class, is the only one of the 32 classes of symmetry which has never yet been observed in actual crystals.

*Class 22.—Ditrigonal Bipyramidal Class. Holohedral-Trigonal Class, or Trigonal Hexagonal-Hemihedral Class. Type, Ditrigonal Equatorial.*

This class exhibits the full trigonal symmetry, namely, a trigonal axis arranged vertically, and three symmetry planes mutually inclined at  $120^\circ$  intersecting in it, thus rendering it ditrigonal; together also with an equatorial plane of symmetry (horizontal, parallel to the basal plane), and three digonal axes lying in it at its intersections with the three vertical symmetry planes.

Only two examples of this class have yet been observed, namely, silver hydrogen phosphate,  $\text{Ag}_2\text{HPO}_4$ , by Dufet in 1886, and benitoite, an acid titano-silicate of barium,  $\text{BaTiSi}_3\text{O}_9$ , by Louderback in 1907. The latter forms beautiful sapphire-blue crystals, which make excellent gem-stones. A later investigation by Jaeger, however, in 1915, would appear to have shown that benitoite is only pseudo-trigonal, and is really optically biaxial.

The general form, the stereographic projection of which is given in Fig. 279, is a **ditrigrinal bipyramid**, which is shown in outline in Fig. 280; it is symmetrical to the equatorial basal plane in which the upper and lower pyramids unite, the shape of which is hexagonal with three more and three less obtuse angles, alternately arranged, corresponding to three larger and three smaller angles over the polar edges of the pyramid. The Millerian indices of this ditrigrinal bipyramid are  $\{pqr\}$ , and the Bravais-Miller indices  $\{h\bar{k}l\}$ . The actual bipyramid shown in both Fig. 279 and Fig. 280 is the form  $\{8\bar{1}4\}$  constructed to scale to the axial ratio of calcite. There is, however, a second form possible, having its poles arranged in pairs adjacent to the negative radii in the Millerian projection instead of the positive radii. The two forms are therefore distinguished as positive and negative respectively. The Millerian indices of the negative form are  $\{p'q'r'\}$ , where  $p' = -p + 2q + 2r$ ,  $q' = 2p - q + 2r$ , and  $r' = 2p + 2q - r$ ; and the Bravais-Miller symbol is  $\{\bar{h}kl\}$ . Thus the positive ditrigrinal bipyramid  $\{20\bar{1}\}$  or  $\{2\bar{1}3\}$  corresponds to the negative, complementary or inverse ditrigrinal bipyramid  $\{425\}$  or  $\{\bar{2}13\}$ . The particular pole of which these latter inverse-form symbols are the facial indices, is the one at an equal distance on the other side of the centre, on the same diameter and in the same upper hemisphere as  $\{20\bar{1}\}$ . (See Figs. 284 and 285 on pages 338 and 339.)

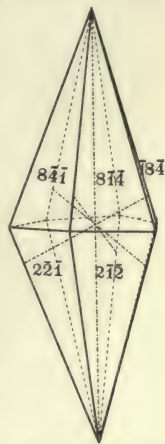


FIG. 280.—Positive Ditrigrinal Bipyramid.

It will be observed in Fig. 280 that the lower faces have altogether different indices to the upper faces;  $\{2\bar{1}2\}$ , for instance, in the case of the lower-right-front face corresponds to  $\{8\bar{1}4\}$  as the indices of the face immediately above it, the face the indices of which are taken for the form symbol  $\{8\bar{1}4\}$ . It will be clear that this must be so, because the lower faces are parallel to the upper faces of the inverse form, and so will have the same numbers for indices as that inverse form, but with the signs all changed. Thus if we calculate the values of  $p'$ ,  $q'$ , and  $r'$  (with the aid of the above formulæ) which correspond to  $p$ ,  $q$ ,  $r$  of the values  $\{8\bar{1}4\}$ , we shall find that  $p' = -18$ ,  $q' = 9$ , and  $r' = 18$ , or, dividing by 9 throughout,  $p' = -2$ ,  $q' = 1$ , and  $r' = 2$ ; hence  $\{2\bar{1}2\}$  are the indices of the inverse face, and if we change the signs we obtain  $\{2\bar{1}2\}$  for the indices of the face parallel to that inverse face, that is, for the indices of the lower-right-front face in Fig. 280, just as they are marked on the face in the drawing.

The three Millerian axes and the vertical trigonal axis are shown in Fig. 280 in broken-and-dotted lines.

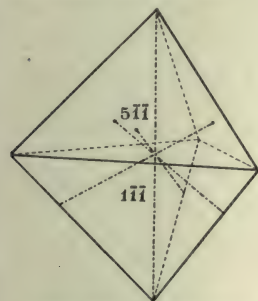


FIG. 281.—Positive First Order Trigonal Bipyramid.

There are six special cases possible, giving rise to as many specific forms.

(1) When the poles lie in the three symmetry planes, each pair having coalesced into a single pole, a **trigonal bipyramid of the first order** is produced. Two varieties are possible, convertible by  $60^\circ$  of rotation, according to which particular three of the six radii in the projection the pairs of poles approach and coalesce on. If they coalesce on the positive radii, as they appear to be about to do in Fig. 279, the positive form is produced; but if they coalesce on the other three, the negative radii, the negative or inverse form is developed. The Millerian indices of the positive form are  $\{pqq\}$ , and the Bravais-Miller indices  $\{h0hl\}$ ; in the case of the negative form the Millerian indices are  $\{p'q'q'\}$ , where  $p' = -p + 4q$ , and  $q' = 2p + q$ , and the Bravais-Miller indices are  $\{\bar{h}0hl\}$ . Thus the inverse or negative

form corresponding to the positive form  $\{5\bar{1}\bar{1}\}$  or  $\{20\bar{2}1\}$  is  $\{\bar{1}11\}$  or  $\{2021\}$ , the two facial poles the indices of which are used in the form symbols being those on the back-and-front diameter, equidistant from the centre, in the upper hemisphere. (See Figs. 284 and 285.) The positive form  $\{5\bar{1}\bar{1}\}$ , drawn for the axial ratio of calcite, is shown in Fig. 281. The indices of the upper faces are  $(5\bar{1}\bar{1})$ , the front face marked in the drawing,  $(\bar{1}5\bar{1})$ , and  $(\bar{1}\bar{1}5)$ . The three lower faces, being parallel to the possible faces of the inverse form  $\{\bar{1}11\}$ , have the indices  $(1\bar{1}\bar{1})$ , the front face marked in Fig. 281,  $(\bar{1}1\bar{1})$ , and  $(\bar{1}\bar{1}1)$ .

(2) The second special case is when the pairs of poles leave the proximity of the symmetry planes and take up a more separated position exactly midway between those planes, that is, at  $30^\circ$  from them. The angles between the faces over all six polar edges then become equal and a **hexagonal bipyramid of the second order** is produced. The Millerian and Bravais-Miller symbols are respectively  $\{pqr\}$  and  $\{h \cdot h \cdot 2h \cdot l\}$ . In the Millerian symbol one index is always the mean of the other two.

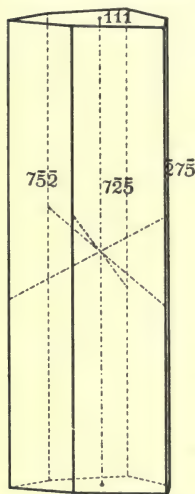


FIG. 282.—Positive Ditrigonal Prism.

(3) The third special case is afforded when the poles remain more or less adjacent to the symmetry planes but lie on the primitive circle. The solid produced is a **ditrigonal prism**, the six faces of which are parallel to the trigonal axis of symmetry. It is shown in Fig. 282, closed by the basal pinakoid. Its symbols are  $\{pqr\}$ , where  $p+q+r=0$ , and  $\{h\bar{k}0\}$ . There are two such forms possible, the one for which the symbols have just been given being the positive form, having its poles adjacent to the positive radii in the projection. The negative form, with poles adjacent to the negative radii, has the symbols  $\{p'q'r'\}$  or  $\{\bar{h}k0\}$ , where  $p'$ ,  $q'$ , and  $r'$  have the values given on the previous page. The one actually shown, drawn to scale to the axial ratio of calcite, is the form  $\{7\bar{2}5\}$ , which is the ditrigonal prism corresponding to the bipyramid  $\{814\}$  shown in Fig. 280. The poles of both prisms and both bipyramids are shown in the stereographic projection Fig. 285.

(4) Just as case (3) corresponds to the ditrigonal bipyramid, so there is another special case of a prism corresponding to (1), namely, the **trigonal prism of the first order**, when the two poles near a symmetry plane coalesce into a single pole lying on the primitive circle at the end of the digonal symmetry axis which is also the projection of the symmetry plane. There are two varieties of this form, a positive and a negative, convertible one into the other by rotation for  $60^\circ$  about the trigonal axis, just as in the case of the pyramid. The symbols of the positive form, the poles of which occupy the positive radii, are  $\{2\bar{1}\bar{1}\}$  and  $\{10\bar{1}0\}$ . It is shown in Fig. 283, closed by the basal pinakoid. The symbols of the negative form are  $\{211\}$  and  $\{\bar{1}010\}$ ; its poles occupy the three negative radii.

(5) This is the special case corresponding to (2), when the poles arranged at  $30^\circ$  from the digonal axes lie on the primitive circle. The result is the **hexagonal prism of the second order**, the symbols of which are  $\{10\bar{1}\}$  and  $\{1120\}$ .

(6) The last special case is when all the six ditrigonal pyramid poles converge towards and coalesce in the centre of the projection, when as the final limiting form the **basal pinakoid** with pole at the centre itself is produced, which in Millerian notation is the parametral form  $\{111\}$  and in Bravais-Miller notation is denoted by the symbol  $\{0001\}$ .

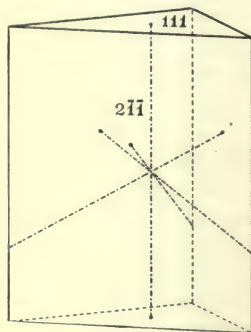


FIG. 283.—Positive First Order Trigonal Prism.



The net result of the above detailed discussion of the possible holohedral trigonal forms is embodied in the following list :

*List of Forms in Class 22.*

$\{111\} = \{0001\}$  Basal pinakoid. 2 faces.

$\{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$  Positive trigonal prism of the first order ;  $\{\bar{2}11\} = \{\bar{1}010\}$  negative trigonal prism of the first order. Each 3 faces.

$\{10\bar{1}\} = \{11\bar{2}0\}$  Hexagonal prism of the second order. 6 faces.

$\{pqr\}$  (where  $p+q+r=0$ ) =  $\{h\bar{k}l0\}$  Positive ditrigonal prism ;  $\{p'q'r'\}$  (where  $\left. \begin{array}{l} p' = -p+2q+2r \\ q' = 2p-q+2r \\ r' = 2p+2q-r \end{array} \right\}$ ) =  $\{\bar{h}kl0\}$  negative ditrigonal prism. Each 6 faces.

$\{pqq\}$  (two indices always equal) =  $\{h0\bar{h}l\}$  Positive trigonal bipyramid of the first order, including the primary positive form  $\{100\} = \{10\bar{1}1\}$  ;  $\{p'q'q'\}$  (where  $\left. \begin{array}{l} p' = -p+4q \\ q' = 2p+q \end{array} \right\}$ ) =  $\{\bar{h}0hl\}$  negative trigonal first order bipyramid, including the complementary primary negative form  $\{\bar{1}22\} = \{\bar{1}011\}$ . Each 6 faces.

$\{pqr\}$  (where one index = mean of other two) =  $\{h . h . 2\bar{h} . l\}$  Hexagonal bipyramid of the second order. 12 faces.

$\{pqr\} = \{h\bar{k}l\}$  Positive ditrigonal bipyramid ;  $\{p'q'r'\}$  (where  $\left. \begin{array}{l} p' = -p+2q+2r \\ q' = 2p-q+2r \\ r' = 2p+2q-r \end{array} \right\}$ ) =  $\{\bar{h}kl\}$  negative ditrigonal bipyramid. Each 12 faces.

The necessity of being familiar with both the Bravais-Miller and the Millerian methods of description of trigonal crystals, owing to the employment of both in current crystallographic work, renders it essential to be perfectly clear as to the mode of deriving the indices of faces and symbols of forms in the two cases, and to have a ready means of converting those of the one into those of the other. The two comparative stereographic projections given in Figs. 284 and 285 show the whole of the facial indices of a considerable number of the principal forms commonly developed on trigonal crystals, including those of all seven types of forms ; Fig. 284 is constructed on the Bravais-Miller system, and Fig. 285 according to Miller's method. In the case of the former, the indices of the poles on the upper hemisphere alone are given, for the poles on the lower hemisphere situated immediately underneath those of the upper hemisphere only differ by the  $c$  index (the last of the four,  $l$ ) being negative instead of positive, the  $A_1$ ,  $A_2$ , and  $A_3$  indices being identical. In the case of the latter projection (Fig. 285) the poles of the lower hemisphere are actually indicated by rings, and as the two symbols are different they are both given, the one above the pole referring to the dot (the upper hemisphere pole) and the symbol below referring to the ring-pole, that of the lower hemisphere. An inspection of them will at once clear up any lingering ambiguity or difficulty arising from the perusal of the preceding description of class 22 forms, and they will be of use also in verifying the general or particular symbols given in connection with the other six classes of the trigonal system. The axial ratio of calcite was used in constructing both figures.

Three extremely useful equations connect the Bravais-Miller and Millerian indices of any face of a trigonal crystal, and these indispensable formulæ may be readily verified in the case of any pole shown on the

two projections just given. As before, three different letters, namely,  $p$ ,  $q$ , and  $r$ , are here employed to represent the Millerian index numbers, to those used for the Bravais-Miller indices,  $h$ ,  $i$ ,  $k$ , and  $l$ , in order that the two kinds of index numbers may at once be identified.

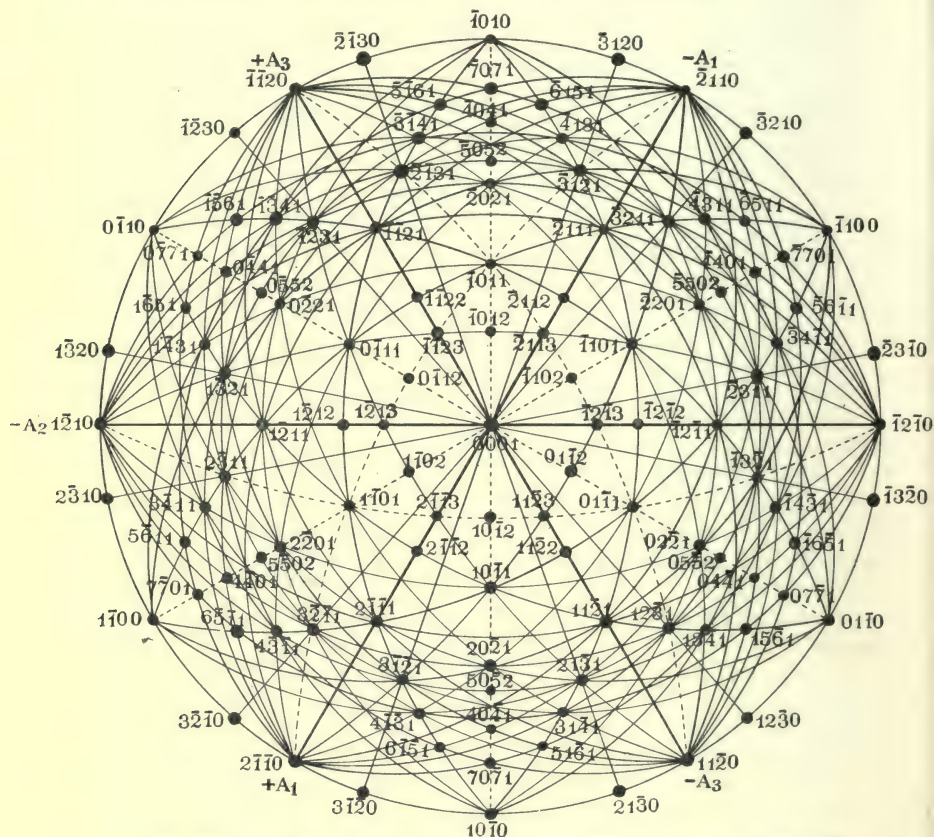


FIG. 284.—Bravais-Miller Stereographic Projection of Trigonal or Hexagonal Forms.

The three connecting equations are :

$$p = h - k + l; \quad q = i - h + l; \quad r = k - i + l.$$

$$h = \frac{p - q}{3}; \quad i = \frac{q - r}{3}; \quad k = \frac{r - p}{3}; \quad l = \frac{p + q + r}{3}$$

Given either the Millerian or the Bravais-Miller indices, the other indices can always be found with the aid of these equations.

*Class 21.—Ditrigonal Scalenohedral Class. Calcite Class.*  
*Rhombohedral Hexagonal-Hemihedral Class. Type, Dihexagonal Alternating.*

This is one of the most important classes of the trigonal system, for it is the class to which calcite, calcium carbonate,  $\text{CaCO}_3$ , and its allied



minerals belong. The elements of symmetry are shown in Fig. 286. They are the essential trigonal axis, three symmetry planes intersecting in it and thus rendering it a ditrigonal axis, and three digonal axes lying in the equatorial plane midway between the symmetry planes,

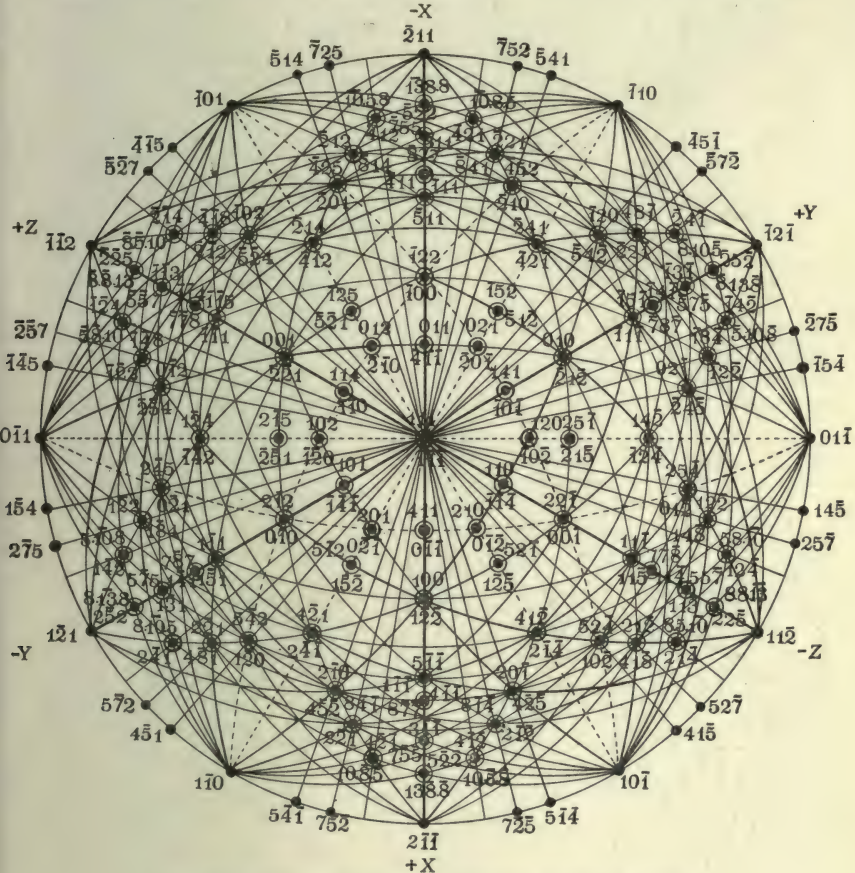


Fig. 285.—Millerian Stereographic Projection of Trigonal Forms.

that is, identical with the three Bravais-Miller hexagonal crystallographic axes. It differs from the holohedral class 22 by having no equatorial plane of symmetry, and in the positions of the digonal axes, these lying in the three symmetry planes in class 22. The operation of the three digonal axes in class 21 has the same effect as if the ditrigonal axis were a hexagonal axis of compound symmetry, that is, a hexagonal axis combined with simultaneous reflection across the equatorial plane. The effect is also to produce centro-symmetry.

The general form the poles of which are shown in Fig. 286 is a twelve-faced solid consisting of two ditrigonal pyramids, an upper one and a lower one, the lower one of which



is rotated for  $60^\circ$  with respect to the upper, round the vertical axis, so that the equatorial junction-edges of the two do not form a simple hexagon, lying in the equatorial plane

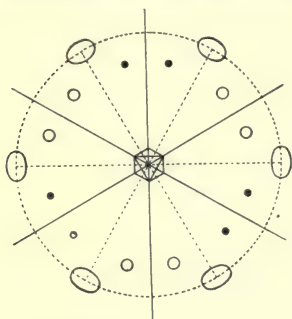


FIG. 286.—Symmetry Elements and General Form of Class 21.

and showing two alternating kinds of angles as in class 22, but is of a zigzag character, above and below the equator. The digonal axes emerge at the centres of the edges forming the zigzag. This general form is the **ditrigrinal scalenohedron**, so called because each face is a scalene triangle. It is shown in Fig. 287, the particular representative being the common form of calcite  $\{20\bar{1}\}$ , drawn to scale to the correct axial ratio for calcite. The polar edges are of two kinds, the angles over them being alternately larger and smaller, as in the case of the ditrigrinal bipyramid of class 22. The scalenohedron possesses in fact the faces of an upper ditrigrinal pyramid  $\{pqr\} = \{h\bar{k}l\}$ , and of the lower parallel ditrigrinal pyramid  $\{\bar{p}\bar{q}\bar{r}\} = \{\bar{h}ikl\}$ . The broken- and -dotted lines indicate the Millerian axes and the vertical

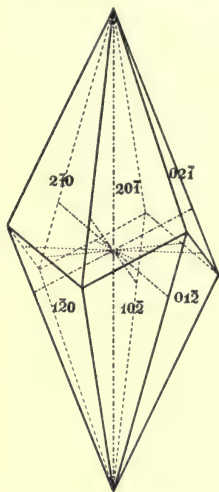


FIG. 287.—Positive Ditrigrinal Scalenohedron.

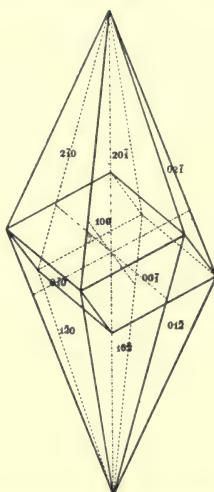


FIG. 288.—Primary Rhombohedron and Scalenohedron of Calcite.

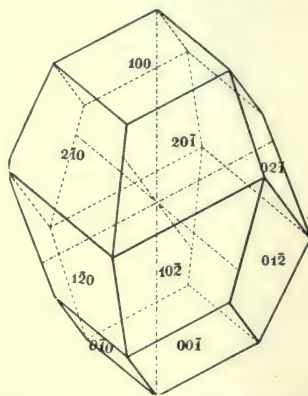


FIG. 289.—Combination of Rhombohedron and Scalenohedron.

of which are adjacent to the negative halves of the axes, and  $60^\circ$  from those of the positive form in the projection. The values of  $p'$ ,  $q'$ , and  $r'$  are those for the inverse forms given in the introduction to this chapter and in the description of class 22, namely,  $p' = -p + 2q + 2r$ ,  $q' = 2p - q + 2r$ ,  $r' = 2p + 2q - r$ .

It is an interesting fact that the zigzag edges of the scalenohedron coincide with the six lateral edges of the rhombohedron, provided the indices bear a certain simple relationship. This occurs in the case of calcite, the common scalenohedron of which  $\{20\bar{1}\}$ , the predominating form of the well-known "dog-tooth" spar, and the primary

rhombohedron  $\{100\}$ , so chosen because it is also a very common form and its facial planes are the cleavage planes of the mineral, have the same zigzag edges, as is shown in Fig. 288. The faces of this scalenohedron consequently bevel the equatorial edges of the primary rhombohedron, as will be still clearer from Fig. 289, which shows a combination almost equally developed of  $\{20\bar{1}\}$  and  $\{100\}$ . Moreover, the hexagonal prism of the second order  $\{10\bar{1}\}$  truncates the edges of either, as is shown in the case of the scalenohedron  $\{20\bar{1}\}$  in Fig. 290, and in the case of the rhombohedron  $\{100\}$  in Fig. 291; in this latter figure the prism is largely developed, its ends being differently terminated by the two halves, upper and lower, of the rhombohedron.

The scalenohedron has one pole in each of the  $30^\circ$  triangles in the projection, which are formed by two radii and the twelfth part of the primitive circle. It will be obvious, therefore, that this general form will have the usual six special cases, in which the pole leaves the inside of the triangle and migrates on to one or other of the six elements of this spherical triangle. These cases will be considered in turn.

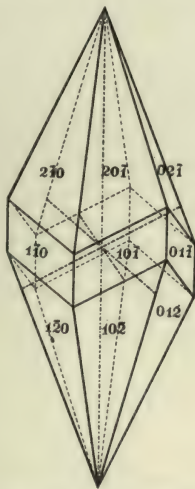


FIG. 290. — Combination of Scalenohedron and Second Order Hexagonal Prism.

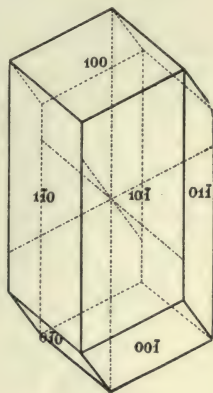
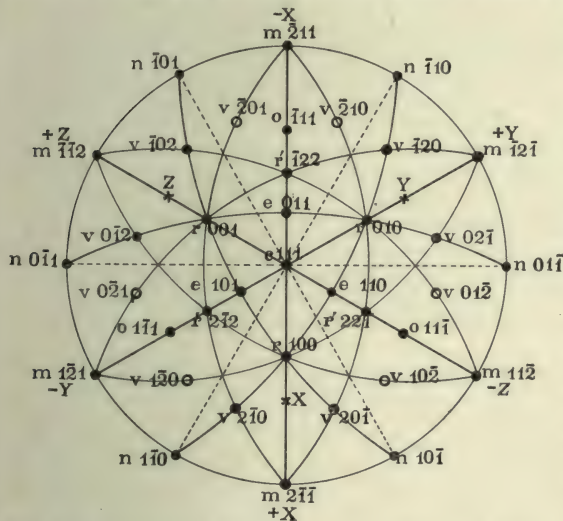


FIG. 291. — Combination of Rhombohedron and Second Order Hexagonal Prism.



fronting the observer; its projection has already been shown in Fig. 273, which represents the primary rhombohedron  $\{100\}$ , and its actual appearance in Fig. 274, in discussing the derivation of the Millerian axes. It is also indicated by the poles  $r$  in Fig. 292. It is reproduced in Fig. 293, the Millerian axes being indicated by the broken-and-dotted lines.

The negative rhombohedron,  $r'$  in Fig. 292, is obtained by rotating the positive one round the vertical trigonal axis for  $60^\circ$  or  $180^\circ$ . It is often called the inverse rhombohedron. Every rhombohedron consists of three pairs of parallel faces, each bounded by four equal sides when evenly developed, and in any case by two pairs of equal sides forming a parallelogram. It may be regarded as a cube deformed by either

compression or elongation along a diagonal. If other rhombohedra are developed on a crystal, besides the primary one  $\{100\}$  chosen as affording the axial planes, and which in the case of calcite is unmistakably the most

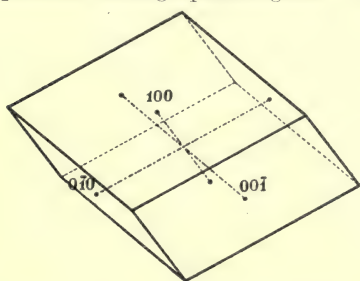


FIG. 293.—Positive Primary Rhombohedron.

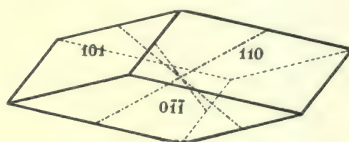


FIG. 294.—Obtuse Negative Rhombohedron.

important one as the mineral cleaves very readily along those planes, they are termed obtuse or acute according as the pole comes between the centre and the pole of  $(100)$  or its inverse  $(2\bar{2}\bar{1})$ , or between either of the latter and the pole  $(2\bar{1}\bar{1})$  or  $(11\bar{2})$  on the primitive circle. Thus  $e = \{110\}$  in Fig. 292 is an obtuse and  $o = \{1\bar{1}\bar{1}\}$  an acute inverse or negative rhombohedron. The obtuse negative rhombohedron  $\{110\}$  is shown in Fig. 294.

The rhombohedron of this class 21 is really a rhombohedron of the first order, and as such is to be clearly distinguished from the more general rhombohedron of the third order which we shall have to consider in class 17; it has always two equal indices, by virtue of the fact that the normal to each face lies in one of the three trigonal planes of symmetry, which renders it symmetrical to the two crystallographic axes lying in the two other planes of symmetry. Indeed the rhombohedron may be considered as built up of two trigonal pyramids the faces of which are parallel to each other; the lower pyramid not being immediately under the upper so as to have a common base, but rotated  $60^\circ$  with respect to it, round the vertical trigonal axis, just as the scalenohedron has been shown to possess the faces of an upper ditrigonal pyramid and of the lower one having faces parallel to it, the parallelism having been brought about by the lower one being rotated  $60^\circ$  with respect to it. The general symbol is therefore that of the trigonal pyramid of the first order, namely,  $\{pqq\}$  in Millerian notation.

The indices of the upper faces of the inverse or negative rhombohedron complementary to the primary one  $\{100\}$  have already been shown in the introduction to this chapter to be  $(2\bar{1}2)$ ,  $(2\bar{2}\bar{1})$ , and  $(\bar{1}22)$ , the form symbol being  $\{\bar{1}22\}$ . In general terms the Millerian symbol of the inverse form is  $\{p'q'r'\}$ , where the usual equations connecting trigonal direct and inverse forms apply, namely,  $p' = -p + 2q + 2r$ ,  $q' = 2p - q + 2r$ ,  $r' = 2p + 2q - r$ . In this special case, where  $q$  and  $r$  are equal, the inverse form is  $\{p'q'q'\}$ , where  $p' = -p + 4q$  and  $q' = 2p + q$ . In Bravais notation the direct (positive) and inverse (negative) forms bear the symbols  $\{h0h\}$  and  $\{\bar{h}0h\}$  respectively.

It is an interesting fact that the cube is the intermediate limiting form between the possible obtuse-angled and acute-angled rhombohedra. In this special case, which is crystallographically possible, the axial ratio on the Bravais-Miller system being  $a : c$



$=1:1.2247$ , the faces of the rhombohedron become squares, and the angles, both over the polar edges and the zigzag middle edges, all right angles; moreover, if the edges were taken for the Millerian axes the axial angles would of course also be right angles, and the lengths of the axes are already equal. But a rhombohedral cube belonging to the trigonal system would at once be distinguished from a true cube of the cubic, optically isotropic or singly-refracting, system by the fact that it would show double refraction, and the phenomenon in convergent polarised light of a single optic axis along a diagonal of the apparent cube. This is an exceptionally striking case of the value of the optical properties, to be fully discussed in later chapters (Part III.), in confirming or even determining the system to which a crystal belongs.

The frequently occurring combination of the primary direct rhombohedron  $\{100\}$  with the hexagonal prism of the first order  $\{2\bar{1}1\}$  is shown in Fig. 295; the upper and lower halves of the rhombohedron form the two different terminations of the prism.

Fig. 296 gives a typical combination of the primary rhombohedron  $r=\{100\}$  with the obtuse

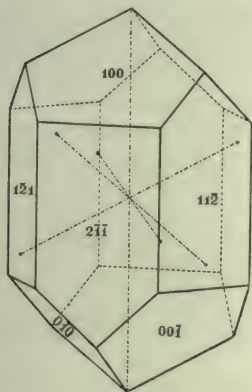


FIG. 295.  
Combination of Rhombohedron  
and First Order Hexagonal Prism.

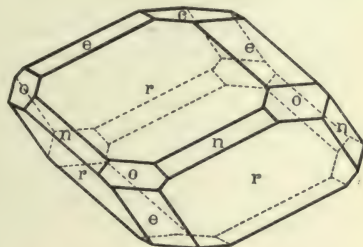


FIG. 296.—Combination of Three Rhombohedra,  
Second Order Hexagonal Prism, and Basal  
Pinakoid.

inverse rhombohedron  $e=\{110\}$ , the acute inverse rhombohedron  $o=\{11\bar{1}\}$ , the hexagonal prism  $n=\{10\bar{1}\}$ , and the basal pinakoid  $c=\{111\}$ . The poles of all these forms are shown in Figs. 292, 284, and 285, as well as those of the primary inverse rhombohedron  $r'=\{22\bar{1}\}$ , the prism  $m=\{2\bar{1}1\}$ , and the positive scalenohedron  $v=\{20\bar{1}\}$ ; in Fig. 292 the poles of emergence of the axes X, Y, and Z, which are marked by a cross in each case, are also given. The axial ratio used in all three projections is that of calcite,  $a:c=1:0.8545$ . The position of these axial poles is readily calculated, for the angle  $mX$ ,  $mY$ , or  $mZ$  is equal to that between the polar edge of the rhombohedron parallel to the axis in question and the equatorial plane, and the tangent of this angle is equal to the axial ratio divided by  $\sqrt{3}$ , that is,  $\tan mX = \frac{c}{a\sqrt{3}}$ . In the case of calcite this gives  $26^\circ 16'$  for  $mX$ . Now this is also the angle  $ce$ , between (111) and (011). Hence the form  $e$  directly replaces the edges of  $r$ .

The predominating primary rhombohedron  $\{100\}$  resembles closely a cube, and the other forms present on the crystal shown in Fig. 296 cause it to appear to be modified by the octahedron and rhombic dodecahedron; if the first-mentioned form could be somewhat elongated parallel to the vertical axis the illusion would be perfect.

The rhombohedron is obviously, therefore, one of the most important of all crystallographic forms.

(2) The second special case occurs when the pole falls on the other kind of diameter in the projection, namely, on one of the digonal axes, at  $30^\circ$  from, and midway between, two crystallographic-axial-plane diameters. The operation of the

three symmetry planes and the three digonal axes then determines that there shall be six such poles in each hemisphere, two immediately above and below each other on each of the digonal axial radii, and the result is consequently a **hexagonal bipyramid of the second order**, which is thus the limiting case of scalenohedra the two kinds of polar angles of which are becoming more and more nearly equal, and the equatorial zigzag edges of which are straightening out until they eventually become the hexagonal section of the hexagonal bipyramid, lying wholly in the equatorial plane. The Bravais-Miller symbol for this form has already been shown to be  $\{h . h . 2\bar{h} . l\}$ . The Millerian symbol is such that one index is always the mean of the other two, and the pole corresponding to the Bravais-Miller symbol just given will be  $\{pqr\}$ .

(3) When the pole lies anywhere on the primitive circle, between the ends of the two axial diameters, the form produced is the **dihexagonal prism**, the Bravais-Miller symbol of which is  $\{h\bar{k}0\}$ , and the Millerian symbol  $\{pqr\}$ , where the sum of  $p$ ,  $q$ , and  $r$  is 0. The dihexagonal prism has invariably two different angles, alternately larger and smaller; for the particular one with equal angles, the section of which would be a regular twelve-sided polygon, is impossible on account of irrationality and the fact that impossible twelve-fold symmetry would thereby be introduced.

(4) When the pole migrates to the end of a crystallographic axial diameter, at its intersection with the primitive circle, the **hexagonal prism of the first order** is produced, the Bravais-Miller symbol being as in the hexagonal system  $\{10\bar{1}0\}$ , and the Millerian symbol being  $\{2\bar{1}\bar{1}\}$ .

(5) When the pole migrates to the end of the other kind of diameter, a digonal axis, the **second order hexagonal prism** is produced,  $\{11\bar{2}0\}$  or  $\{10\bar{1}\}$ .

(6) Finally, when the pole migrates to the remaining element of the spherical triangle, the intersection of two axial radii at the centre, that is, to that corner of the triangle which occupies the centre of the primitive circle and of the whole projection, the **basal pinakoid** is produced,  $\{0001\}$  or  $\{111\}$ .

To summarise, we have the following forms in this class :

*List of Forms in Class 21.*

$\{111\} = \{0001\}$  Basal pinakoid. 2 faces.

$\{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$  Hexagonal prism of the first order. 6 faces.

$\{10\bar{1}\} = \{11\bar{2}0\}$  Hexagonal prism of the second order. 6 faces.

$\{pqr\}$  (where  $p+q+r=0$ ) =  $\{h\bar{k}0\}$  Dihexagonal prism. 12 faces.

$\{pq\bar{q}\}$  (two indices always equal) =  $\{h0\bar{h}l\}$  Positive or direct rhombohedron of the first order, including the primary rhombohedron  $\{100\} = \{10\bar{1}1\}$ ;  $\{p'q'q'\}$  (where  $\begin{cases} p' = -p+4q \\ q' = 2p+q \end{cases}$ ) =  $\{\bar{h}0hl\}$  negative or inverse rhombohedron of the first order, including the complementary inverse primary one  $\{\bar{1}22\} = \{\bar{1}011\}$ . Each 6 faces.

$\{pqr\}$  (where one index = the mean of the other two) =  $\{h . h . 2\bar{h} . l\}$  Hexagonal bipyramid of the second order. 12 faces.

$\{pqr\} = \{h\bar{k}l\}$  Positive ditrigonal scalenohedron.  $\{p'q'r'\}$  (where  $p' = -p+2q+2r$ ,  $q' = 2p-q+2r$ ,  $r' = 2p+2q-r$ ) =  $\{\bar{h}kl\}$  negative ditrigonal scalenohedron. Each 12 faces.

By far the most important substance crystallising in this class of the trigonal system is calcite,<sup>1</sup> calc spar, or Iceland spar, carbonate of lime,  $\text{CaCO}_3$ . The name Iceland spar is usually confined to the primary rhombohedral variety (Fig. 293) of the clear transparent mineral, which has in the past been found in large pieces, the original discovery having occurred in the seventeenth century at Eskifjörður, a cavity of 6000

<sup>1</sup> For the structure of calcite as revealed by X-rays see Chapter XXXIII.

cubic feet (40 feet long, 15 feet wide, and 10 feet high), in a lava bed of doleritic basalt, having been found filled with rhombohedra and scalenohedra of calc spar. The crystals were often two feet or more in size, and although rough and dull on their exterior, were remarkably clear, colourless, and flawless within. Large crystals are now becoming rare and exceedingly valuable on account of the use of the spar for polarising purposes in the Nicol prism. This well-known piece of optical apparatus is simply a cleavage rhomb of calc spar parallel to the faces of the primary rhombohedron  $\{100\}$ , cut along a certain diagonal direction into two halves, which are subsequently cemented together again by Canada balsam in such a manner as to eliminate by total reflection one of the two rays of polarised light into which ordinary light is divided when it enters the spar, thus allowing the other ray to pass out alone as a beam of plane polarised light. A detailed description of it will find its proper place in Chapter XL.

In the next chapter a crystal of calcite will be goniometrically described in detail, as an example of trigonal measurements and calculations. Figs. 287 (scalenohedron  $\{20\bar{1}\}$ ), 289 (rhombohedral  $\{100\}$  and scalenohedron  $\{20\bar{1}\}$ ), 290 (scalenohedron  $\{20\bar{1}\}$  and second order hexagonal prism  $\{10\bar{1}\}$ ), 291 (rhombohedral  $\{100\}$  and second order hexagonal prism  $\{10\bar{1}\}$ ), 295 (rhombohedral  $\{100\}$  and first order hexagonal prism  $\{2\bar{1}\bar{1}\}$ ), and the rich rhombohedral combination shown in Fig. 296 all represent calcite crystals, drawn exactly in accordance with the correct axial ratio. The stereographic projections given in Figs. 284, 285, 292, and 327 (next chapter) all refer to calcite.

Also belonging to this class 21 are ruby and sapphire, the two beautiful crystalline varieties of corundum,<sup>1</sup> alumina,  $\text{Al}_2\text{O}_3$ , so much prized as gem-stones, ruby being the red variety and sapphire the blue variety. The colour is due to minute quantities of ferric oxide. The crystals are composed of the four forms  $\{10\bar{1}\}$  second order hexagonal prism,  $\{111\}$  basal pinakoid,  $\{100\}$  primary first order rhombohedron, and  $\{3\bar{1}\bar{1}\}$  a second order hexagonal bipyramid. The latter form is characteristic of the sapphire, and is rarely present on the ruby, which latter is usually tabular parallel to the basal pinakoid  $\{111\}$ . Corundum is occasionally found in small perfectly colourless crystals exhibiting the same forms just enumerated. Brown and yellow varieties are fairly common, and are known as oriental topaz; while a green variety is sometimes found, termed oriental emerald, and also a purple variety which is known as oriental amethyst.

Specular iron ore,<sup>1</sup> hæmatite,  $\text{Fe}_2\text{O}_3$ , also crystallises with class 21 symmetry.

*Class 20.—Ditrigonal Pyramidal Class.—Tourmaline Class.*

*Hemimorphic-Hemihedral Class. Type, Ditrigonal Polar.*

This class possesses only the three symmetry planes and the essential trigonal (here consequently ditrigonal) axis in which they intersect.

<sup>1</sup> For the structure of corundum and hæmatite as revealed by X-rays see Chapter XXXIII.



Hence the two ends of this axis may exhibit quite different forms. Fig. 297 will render the nature of the symmetry clear.

The general form is obviously a simple **ditrigrinal pyramid**, the edges of which lie in the symmetry planes, exactly like the upper or lower half of either of the ditrigrinal bipyramids of class 22 already described. It is shown in Fig. 298, closed below by the basal plane. The upper form represented in the figure has the symbols  $\{pqr\}$  and  $\{\bar{h}\bar{k}\bar{l}\}$ , and the lower one with faces parallel to it is denoted by  $\{\bar{p}\bar{q}\bar{r}\}$  (that is, the signs of  $p$ ,  $q$ , and  $r$  are the opposite of what they are for the upper form) and  $\{\bar{h}\bar{k}\bar{l}\}$ . This upper form having its pairs of poles adjacent to the positive radii in the projection, and the lower form parallel to it, are termed positive. There are also two negative forms of similar character parallel to each other, the poles of the upper of which lie in

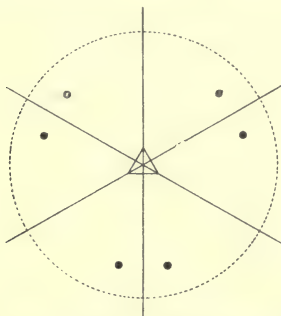


FIG. 297.—Symmetry Elements and General Form of Class 20.



FIG. 298.—Positive Upper Ditrigrinal Pyramid.

pairs adjacent to the negative radii. This negative upper form has the symbols  $\{p'q'r'\}$  and  $\{\bar{h}\bar{k}\bar{l}\}$ , and the lower negative form parallel to it has the symbols  $\{\bar{p}'\bar{q}'\bar{r}'\}$  and  $\{\bar{h}\bar{k}\bar{l}\}$ , where  $p' = -p + 2q + 2r$ ,  $q' = 2p - q + 2r$ ,  $r' = 2p + 2q - r$ . Thus there are four such pyramids possible altogether, having different symbols.

The special cases lead to the following forms :

(1) When the pairs of poles coalesce into single poles lying in the symmetry planes the 3-faced **trigrinal pyramid of the first order** is produced, which occurs in four varieties corresponding to the four ditrigrinal pyramids, and which are similarly distinguished as upper and lower positive and upper and lower negative. The positive

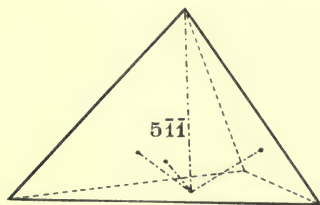


FIG. 299.—Positive Upper Trigrinal Pyramid of the First Order.

upper form, closed by the basal plane, is shown in Fig. 299. In this form two of the indices are always equal, so that the general symbol is  $\{pq\bar{q}\}$ , and although this is the same symbol as that of the rhombohedron of class 21, this form is not a rhombohedron, as only half the faces of the latter are comprised in the form. It may with some ground be regarded as a hemihedral form of the rhombohedron, and consequently as a tetartohedral form of the hexagonal system. There is, however, no necessity to consider it as either, but merely as the first special case of the general

form conforming to that type of homogeneous structure which has the symmetry of class 20. Its faces are perpendicular to the three planes of symmetry. The indices of all four modifications are given in the list of forms.

(2) If each pair of poles adjacent to a symmetry plane separate further, until they reach the intermediate positions  $30^\circ$  from the neighbouring symmetry planes, when

the two different alternate angles over the polar edges become equal, the **hexagonal pyramid of the second order** is produced. As explained under class 21, this occurs when one of the indices is the mean of the other two, so that the Millerian symbol is  $\{pqr\}$  where  $p$ ,  $q$ , and  $r$  have this relationship. There is an upper and a lower variety of this form, owing to the polarity of the vertical axis.

(3) When the poles of the general pyramid migrate on to the primitive circle we have the **ditrigonal prism** produced, already shown in Fig. 282, under class 22. It is a six-sided prism parallel to the trigonal axis, exhibiting two alternate kinds of angles. Its symbol is  $\{pqr\}$  where  $p+q+r=0$ , or  $\{h\bar{k}0\}$ . There are two such prisms possible, the one the symbols of which have just been given being derived from the upper positive or lower negative ditrigonal pyramids; the second variety, derived from the upper negative and lower positive pyramids, has its sharper angle in front and the more obtuse dihedral angle behind.

(4) When each pole is situated at the positive end of a diameter which forms the projection of a symmetry plane, the 3-faced **positive trigonal prism of the first order** is produced, which was described and illustrated in Fig. 283, under class 22. Its symbols are  $\{2\bar{1}1\}$  and  $\{10\bar{1}0\}$ . When the poles are at the negative ends of the diameters, thus occupying the other alternate radial intersections with the primitive circle at  $60^\circ$  from the positive ones, the **negative trigonal prism** is produced,  $\{\bar{2}11\}$  or  $\{\bar{1}010\}$ .

(5) When the poles on the primitive circle are intermediate between the symmetry-plane diameters, at  $30^\circ$  from each, the **hexagonal prism of the second order** is produced,  $\{10\bar{1}\}$  or  $\{11\bar{2}0\}$ .

(6) When the pole occupies the centre of the projection, which is the common sixth element of all the spherical triangles under consideration, formed by the axial radii and the primitive circle, the **basal plane** is produced. Owing to the absence both of the equatorial plane of symmetry and of any digonal axes lying in it, this form is truly described as a plane and not as a pinakoid, for it consists of a single face, the two parallel faces being separate forms. The upper basal plane or pedion is denoted by  $\{111\}$  or  $\{0001\}$ , and the lower one by  $\{\bar{1}\bar{1}\bar{1}\}$  or  $\{000\bar{1}\}$ .

#### *List of Forms in Class 20.*

$\{111\} = \{0001\}$  Upper basal plane or pedion;  $\{\bar{1}\bar{1}\bar{1}\} = \{000\bar{1}\}$  lower basal plane or pedion. Each 1 face.

$\{2\bar{1}1\} = \{10\bar{1}0\}$  Positive trigonal prism of the first order;  $\{\bar{2}11\} = \{\bar{1}010\}$  negative trigonal prism. Each 3 faces.

$\{10\bar{1}\} = \{11\bar{2}0\}$  Hexagonal prism of the second order. 6 faces.

$\{pqr\}$  (where  $p+q+r=0$ ) =  $\{h\bar{k}0\}$  Positive ditrigonal prism;  $\{p'q'r'\}$  where

$$\begin{cases} p' = -p + 2q + 2r \\ q' = 2p - q + 2r \\ r' = 2p + 2q - r \end{cases} = \{\bar{h}i\bar{k}0\} \text{ negative ditrigonal prism. Each 6 faces.}$$

$pqq$  (two indices always equal) =  $\{h0\bar{h}l\}$  Upper positive trigonal pyramid of the first order;  $\{\bar{p}\bar{q}\bar{q}\} = \{\bar{h}0h\bar{l}\}$  lower (parallel to upper) positive trigonal pyramid;  $\{p'q'q'\} = \{h0h\bar{l}\}$  upper negative trigonal pyramid;  $\{\bar{p}'\bar{q}'\bar{q}'\} = \{\bar{h}0h\bar{l}\}$  lower (parallel to upper) negative trigonal pyramid. Each 3 faces.

$\{pqr\}$  (where one index = mean of other two) =  $\{h.h.\bar{2}h.l\}$  Upper hexagonal pyramid of the second order;  $\{\bar{p}\bar{q}\bar{r}\} = \{\bar{h}.\bar{h}.2h.\bar{l}\}$  (or  $\{h.h.\bar{2}h.\bar{l}\}$  the symbol used for this form in the hexagonal system, both faces indicated by the symbols belonging to the form) lower form of same. Each 6 faces.

$\{pqr\} = \{h\bar{k}l\}$  Upper positive ditrigonal pyramid;  $\{\bar{p}\bar{q}\bar{r}\} = \{\bar{h}i\bar{k}l\}$  lower (parallel to upper) positive ditrigonal pyramid;  $\{p'q'r'\} = \{\bar{h}i\bar{k}l\}$  upper negative ditrigonal pyramid;  $\{\bar{p}'\bar{q}'\bar{r}'\} = \{h\bar{k}l\}$  lower (parallel to upper) negative ditrigonal pyramid. Each 6 faces.

The mineral tourmaline,  $\text{H}_6\text{Na}_2\text{Fe}_4\text{B}_6\text{Al}_3\text{Si}_{12}\text{O}_{63}$ ,—so well known from its property of transmitting only one of the two polarised rays into which light traversing it is divided, and absorbing the other, so that a plate of the mineral may be employed for experiments requiring a beam of plane polarised light,—is an excellent example of a substance crystallising in this class. It exhibits prominently the phenomenon of oppositely polar pyro-electricity (see page 355 and Chapter LIX.), being the first substance discovered to possess this remarkable property. Fig. 300 shows a typical crystal of tourmaline, as described by Kuppfer, on which are developed the forms  $m = \{112\}$  (the negative trigonal prism of the first order),  $n = \{10\bar{1}\}$  (the hexagonal prism of the second order),  $r = \{100\}$ ,  $-r = \{1\bar{0}0\}$ ,  $o = \{11\bar{1}\}$ ,  $s = \{1\bar{1}0\}$ ,  $-c = \{1\bar{1}\bar{1}\}$ , and  $v = \{20\bar{1}\}$ . The broken letters in the figure refer to the back faces indicated as usual by the dotted lines. The poles of all these faces are given on the stereographic projections in Figs. 284 and 285, and all but those of  $s = \{1\bar{1}0\}$  in Fig. 292. The upper end of the vertical trigonal axis, as the crystal is drawn in the illustration, is the antilogous pole. The two ends are clearly hemimorphic, certain distinct forms being characteristic of each.

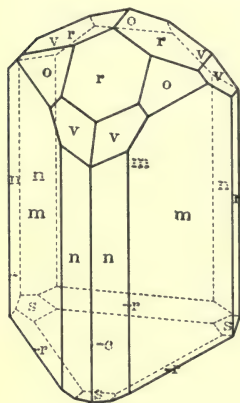


FIG. 300.  
Crystal of Tourmaline.

The Millerian axial angle  $\alpha$  of tourmaline is  $113^\circ 58'$ , and the Bravais-Miller axial ratio  $a : c = 1 : 0.4474$ .

The complicated chemical composition of tourmaline has given rise to much discussion, and the formula given above, while exhibiting the main elements present in a form accepted by leading mineralogists, has been more simply generalised by Penfield and Foote as  $\text{H}_{20}\text{Si}_4\text{B}_2\text{O}_{21}$ , the hydrogen being understood to be more or less replaced by metals. This general formula has been confirmed by H. E. Boecke (*Jahrb. Min.*, 1916, ii. 109), as the result of 54 new analyses of tourmalines. He finds that the  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  are always present in the proportion of 4 to 1.

On account of the importance of this mineral, optically and electrically as well as crystallographically, this class is generally known as the "tourmaline class."

*Class 19.—Trigonal Bipyramidal Class. Trigonal-Tetartohedral Class. Type, Trigonal Equatorial.*

This class is the only one of the 32 classes not yet known to be represented by any actual crystallised substance. It is the third of the possible trigonal classes obtained by adding to the simple trigonal pyramid of the third order,—the poles of which are shown in Fig. 272, and which is the open figure possessing the extreme minimum of trigonal symmetry, namely, a trigonal axis only,—the three faces of another similar pyramid but with faces directed with their apex downwards instead



of upwards. In class 19 the lower pyramid is so arranged that the faces are precisely underneath those of the upper pyramid, the poles on the projection being ringed dots, and the two pyramids having a common equilaterally triangular base.

The poles of the general form of class 19 thus produced are shown in Fig. 301. The only other symmetry element present in the class, besides the essential trigonal axis, is thus the equatorial plane of symmetry.

It will be obvious that this general form is a **trigonal bipyramid of the third order**. It can occur in four varieties, only distinguishable, however, from each other or from the trigonal bipyramid of the first order shown in Fig. 281, so long as their positions of derivation are retained, and convertible into each other by rotation round the trigonal axis. These four varieties may be distinguished as (1) the **right positive**, the form the poles of which are given in Fig. 301 ; (2) the **left positive**, the poles of which

are situated at an equal distance on the other side of the positive radii in each case, and which together with the right positive poles make up the positive ditrigonal bipyramid of the holohedral class 22 ; (3) the **right negative**, the faces of which are parallel to those of the right positive ; its poles are on the right of the negative axial radii, that is, any particular pole will be on the right when the projection is rotated so as to bring the particular radius to which it is adjacent

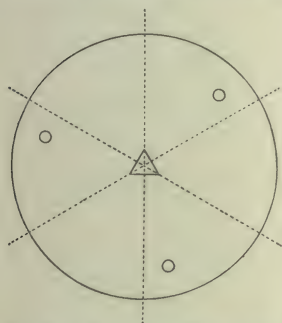


FIG. 301.—Symmetry Elements and General Form of Class 19.

to front the observer ; and finally, (4) the **left negative** modification with a pole on the other side of each negative half of the axes. Varieties (3) and (4) together make up the negative ditrigonal bipyramid. The symbols of these four forms are all given in the list which concludes the description of the class. The  $\{20\bar{1}\}$  representative of the first of the four, the right positive, corresponding to the projection in Fig. 301, is shown in Fig. 302. The lower faces have the "inverse" symbols, the indices of the lower front face being (425).

**Special Cases.**—(1) When the poles fall on the axial radii themselves the **two trigonal bipyramids of the first order** are produced, exactly as in the case of the holohedral class 22 ; the right and left positive trigonal bipyramids of the third order yield the **positive trigonal bipyramid of the first order**, and the right and left negative ones the **negative trigonal bipyramid of the first order**.

(2) When the poles are on the diameters at  $30^\circ$  from the Millerian axial-trace diameters, that is, on the Bravais-Miller axes, the **trigonal bipyramid** becomes one of the **second order**. Two such are possible, a **right** form and a **left**, the right positive third order bipyramid or the left negative leading to the former, and the left positive or right negative to the latter.

(3) When the pole is on the primitive circle, in general a **trigonal prism of the third order** is produced, which may be of four kinds, corresponding to the four third

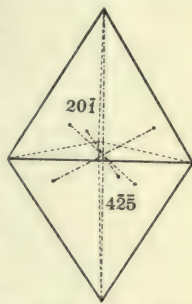


FIG. 302.—Right Positive Third Order Trigonal Bipyramid.

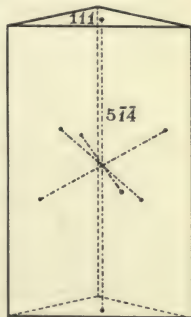


FIG. 303.—Right Positive Trigonal Prism of the Third Order.

order bipyramids, according as it is right or left of the positive or the negative axial radii. The one corresponding to the right positive bipyramid shown in Fig. 302 is given in Fig. 303, closed by the basal pinakoid. Its symbol is  $\{5\bar{1}4\}$ .

(4) When the pole is on the primitive circle and at the end of a positive radius a **positive trigonal prism of the first order** is produced; if at the end of a negative radius the **negative** form is obtained.

(5) When the prismatic pole is midway between the two kinds of diameters, that is, at the end of a Bravais-Miller axial diameter, a **right or left trigonal prism of the second order** is produced.

(6) Finally, when the pole is at the inner corner of the fundamental spherical triangle, that is, at the centre of the whole projection, the **basal pinakoid** is produced.

The symbols of the whole of these forms are set forth in the following list:

*List of Forms in Class 19.*

$\{111\} = \{0001\}$  Basal pinakoid. 2 faces.

$\{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$  Positive trigonal prism of the first order;  $\{211\} = \{\bar{1}010\}$  negative form of same. Each 3 faces.

$\{10\bar{1}\} = \{1120\}$  Right trigonal prism of the second order;  $\{1\bar{1}0\} = \{2\bar{1}\bar{1}0\}$  left form of same. Each 3 faces.

$\{pqr\}$  (where  $p+q+r=0$ ) =  $\{h\bar{k}0\}$  Right positive trigonal prism of the third order;  $\{pq\bar{q}\}$  (same values) =  $\{k\bar{h}0\}$  left positive form of same;  $\{p'q'r'\}$  (where  $\left. \begin{array}{l} p' = -p+2q+2r \\ q' = 2p-q+2r \\ r' = 2p+2q-r \end{array} \right\} = \{\bar{h}k0\}$  right negative form;  $\{p'r'q'\}$  (same values) =  $\{\bar{k}ih0\}$  left negative form. Each 3 faces.

$\{pqq\}$  (two indices always equal) =  $\{h0\bar{h}l\}$  Positive trigonal bipyramid of the first order, including the primary positive  $\{100\} = \{10\bar{1}1\}$ ;  $\{p'q'q'\}$  (where  $\left. \begin{array}{l} p' = -p+4q \\ q' = 2p+q \end{array} \right\} = \{\bar{h}0hl\}$  negative form of same, including the complementary primary negative  $\{\bar{1}22\} = \{\bar{1}011\}$ . Each 6 faces.

$\{pqr\}$  (where one index = mean of other two) =  $\{h . h . 2h . l\}$  Right trigonal bipyramid of the second order;  $\{pq\bar{q}\}$  (same values) =  $\{2h . \bar{h} . \bar{h} . l\}$  left form of same. Each 6 faces.

$\{pqr\} = \{h\bar{k}l\}$  Right positive trigonal bipyramid of the third order;  $\{pq\bar{q}\}$  (same values) =  $\{k\bar{h}l\}$  left positive form of same;  $\{p'q'r'\}$  (where  $\left. \begin{array}{l} p' = -p+2q+2r \\ q' = 2p-q+2r \\ r' = 2p+2q-r \end{array} \right\} = \{\bar{h}k\bar{l}\}$  right negative form;  $\{p'r'q'\}$  (same values) =  $\{\bar{k}ihl\}$  left negative form. Each 6 faces.

*Class 18.—Trigonal Trapezohedral Class. Quartz Class. Hexagonal Trapezohedral-Tetartohedral Class. Type, Trigonal Holoaxial.*

This is another interesting class of the trigonal system, inasmuch as it is the type of symmetry exhibited by the very important and universally occurring mineral quartz, rock crystal, the common crystallised form of silica,  $\text{SiO}_2$ . The elements of symmetry are all axes, there being no plane of symmetry present. The essential trigonal axis is accompanied by three digonal axes lying in the equatorial plane, identical in position with the three horizontal Bravais-Miller axes. The result is that the trigonal pyramid, produced in the upper hemisphere from the general pole ( $pqr$ ) by the operation of the trigonal axis, is accompanied owing to the operation of the digonal axes by a similar trigonal pyramid

in the lower hemisphere, not immediately underneath, however, as in class 19 just considered, but rotated round the trigonal axis with respect to the upper one, so that the poles of these lower hemisphere faces are arranged in the projection symmetrically on the other side of the digonal axes. For it will be obvious that the operation (rotation for  $180^\circ$  round it) of each of the three digonal axes will cause a symmetrical repetition of any given neighbouring pole, in the other hemisphere.

If we start as just mentioned with the usual generally situated pole ( $pqr$ ), namely, one within the fundamental spherical triangle to the right of the front positive axial



FIG. 304.

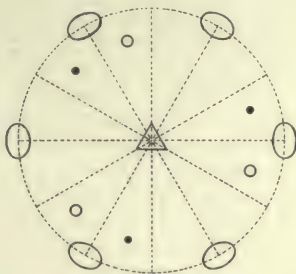


FIG. 305.

Symmetry Elements and Right and Left General Forms of Class 18.

radius, this repetition gives rise to the general form  $\{pqr\}$  just described, and the projection of which is shown in Fig. 275 already given in the introduction to this chapter, and repeated here in Fig. 304 for the reader's convenience. The upper faces are those of the upper half of the right positive bipyramid of the third order of the last class, 19, and the three lower faces resemble the lower half of that solid, but rotated against the upper half round the vertical axis, so that the poles of the two halves lie in the projection symmetrically to the digonal axes, although one pole is a dot and the other a ring in each case. If we were to start instead with the upper half of the left positive third order trigonal bipyramid, we should get by a similar repetition

in the lower hemisphere the six-faced solid the projection of which is shown in Fig. 305, and which is the enantiomorphous counterpart of Fig. 304. As the rotation involves the production of two unequal zigzag edges instead of each horizontal basal edge of the trigonal bipyramid, a trapezoid shape is given to each face, and the solid is termed a **trigonal trapezohedron**. The one corresponding to Fig. 304 is shown in Fig. 306, and the other, the projection of which is given in Fig. 305, is shown in Fig. 307. The first is a **right positive trigonal trapezohedron**, and the second a **left positive**. The Millerian symbols

of the two are  $\{pqr\}$  and  $\{prq\}$ , and the Bravais-Miller symbols  $\{h\bar{k}l\}$  and  $\{k\bar{h}l\}$ , as in the case of the class 19 third order bipyramid the upper faces of which these

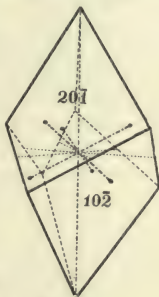


FIG. 306.  
Right Positive Tri-  
gonal Trapezohedron.

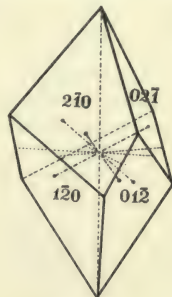


FIG. 307.  
Left Positive Tri-  
gonal Trapezohedron.



trapezohedra possess. These two trigonal trapezohedra are truly enantiomorphous, not being mutually convertible by rotation. Besides these two positive trapezohedra, there are two similar negative ones, corresponding to the two negative trigonal pyramids. Their symbols are, for the **right negative** form  $\{p'r'q'\}$  where  $p'$ ,  $q'$ , and  $r'$  have the usual significations of inverse indices, or  $\{\bar{h}ikl\}$ ; and for the **left negative** form  $\{p'r'q'\}$  or  $\{kihil\}$ . It will be remembered that in order to calculate the inverse facial indices, we employ the equations:

$$p' = -p + 2q + 2r, \quad q' = 2p - q + 2r, \quad r' = 2p + 2q - r.$$

The two negative forms are also truly enantiomorphous between themselves, but they may be converted into the two positive forms by rotation of  $60^\circ$  or  $180^\circ$  about the vertical trigonal axis. Hence there are not four enantiomorphous forms but two, a **right** and a **left**, although there are four distinct forms as derived *in situ*, having the four different symbols already just enumerated. It is an interesting fact that the optically active crystals of this class, of which quartz is an excellent and important example, do not exhibit both a right and a left trigonal trapezohedron on any one crystal, but only a right or a left form. In the case of quartz the type of crystal which rotates the plane of polarisation to the right bears also a face or faces of the right trapezohedron, while the left-handed optical variety bears the left trigonal trapezohedron.

**Special Cases.**—(1) When the pole ceases to be a general one within the spherical triangle and migrates on to one of the Millerian crystallographic axial radii, which bisect the angles between the digonal axial radii, the result is the **first order rhombohedron**  $\{pqq\} = \{h0\bar{h}l\}$ , the same as is so characteristic of the calcite class. Both the right and left positive trigonal trapezohedra have for their limiting case the **positive or direct rhombohedron**, and similarly the right and left negative trapezohedra both coalesce into the **negative or inverse rhombohedron**  $\{p'q'q'\} = \{\bar{h}0hl\}$ , where  $p'$  and  $q'$  have the usual inverse values. Consequently both rhombohedra may be developed on either right-handed or left-handed crystals of this class, as frequently happens in the case of quartz. With regard to the form symbols  $\{pqq\}$  and  $\{p'q'q'\}$ , it should be pointed out that these are the symbols of the faces the poles of which lie on the two halves of the X Millerian axial diameter; the faces with poles on the Y diameter are  $\{qpp\}$  and  $\{q'p'p'\}$ , and those with poles on the Z diameter are  $\{qpp\}$  and  $\{q'q'p'\}$ . Owing to the equality of two indices, the formulæ above quoted for the calculation of the inverse forms in each case simplify to 2 equations each involving two quantities.

(2) When the general pole falls on the digonal axis, the other pole brought in by the operation of that axis falls also on it as a ring, so that a pair of poles vertically over each other occur on each of the three radii in question. The resulting solid is a **trigonal bipyramid of the second order**. The form derived from the right positive trapezohedron of Fig. 306 is the **right trigonal bipyramid**, and the left negative trapezohedron gives rise to the same bipyramid. An analogous **left trigonal bipyramid of the second order** is yielded by the concentration on the three other digonal axial radii of the poles of the left positive and right negative trapezohedra. The symbols are the same as those of the last class (19), and are given in the list of forms. The right trigonal bipyramid of the second order  $\{41\bar{2}\}$  is represented in Fig. 308. The Millerian and vertical axes are shown in broken-and-dotted lines, and the digonal axes in thin dotted lines.

(3) The limiting form of more and more acute trapezohedra is reached when the poles fall on the primitive circle, a **ditrigonal prism** resulting; the right positive and left negative trapezohedra both yielding the same prismatic form, which may be distinguished as the "**right**" one, while the left positive and right negative unite in producing a second ditrigonal prism, which is most conveniently called a "**left**" form. The right ditrigonal prism  $\{514\}$ , corresponding to the right positive trapezohedron  $\{20\bar{1}\}$  (Fig. 306), is shown in Fig. 309. The Millerian and vertical axes and the digonal axes are discriminated as in Fig. 308. It is arranged with its alternately flatter and

sharper angles in the correct positions, as derived. The complementary form would have these angles inverted, the sharper coming in front instead of the flatter. The relations of the two forms can at once be clearly understood by imagining the poles in the two Figs. 304 and 305 carried out (moving along radii) on to the primitive circle. The one prism is convertible into the other by rotation round the vertical trigonal axis for  $60^\circ$  or  $180^\circ$ .

(4) When the poles of the ditrigonal prism separate until they lie at the ends of the Millerian axial radii, the **hexagonal prism of the first order** is produced; or the case may be stated in the form that when the general pole migrates to the end of the adjacent Millerian axis, the operation of the digonal axis at  $30^\circ$  from the latter requires a second pole to be situated at the end of the Millerian axial radius on the other side, also at  $30^\circ$ , from that digonal axis, and this occurring also at the two other pairs of Millerian radii, six prismatic faces are produced at regular intervals of  $60^\circ$ , the particular hexagonal prism produced being that of the first order. Both ditrigonal prisms naturally give rise to the same hexagonal prism of the first order, as there is but one such form possible. This form, consequently, may be equally developed on right-handed or left-handed crystals.

(5) If, however, the two poles of the ditrigonal prism approach each other and

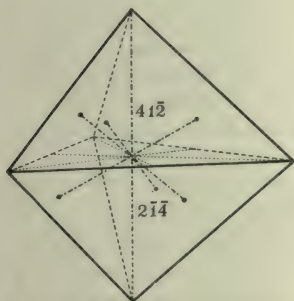


FIG. 308.—Right Trigonal Bipyramid of the Second Order.



FIG. 309.—Right Ditrigonal Prism.

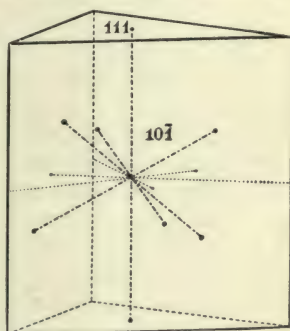


FIG. 310.—Right Trigonal Prism of the Second Order.

eventually concentrate and coalesce on the intersection of the digonal axis with the primitive circle, the prism produced is a trigonal one. The right positive and left negative trapezohedra, or the right ditrigonal prism, all yield the **right trigonal prism of the second order**  $\{10\bar{1}\}$ , which is represented in Fig. 310, closed by the basal pinakoid  $\{111\}$ . The Millerian and vertical axes are drawn in thick broken-and-dotted lines, and the digonal axes in thin dotted lines. The left positive and right negative trapezohedra both yield, as does also the left ditrigonal prism, the **left second order trigonal prism**  $\{1\bar{1}0\}$ , the facial poles of which occupy the other ends of the three digonal axes inverse to those occupied by the right form. These two forms never appear on the same right-handed or left-handed crystal, but only the right form on the right-handed and the left form on the left-handed variety.

(6) When the general pole migrates to the centre of the projection the **basal pinakoid**  $\{111\}$  is produced, both faces  $(111)$  and  $(\bar{1}\bar{1}\bar{1})$  being in the form, on account of the operation of one or all three of the digonal axes.

The forms now shown to be possible to the class are summarised in the following list:

*List of Forms in Class 18.*

- $\{111\} = \{0001\}$  Basal pinakoid. 2 faces.  
 $\{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$  Hexagonal prism of the first order. 6 faces.

- $\{10\bar{1}\} = \{11\bar{2}0\}$  Right trigonal prism of the second order;  $\{1\bar{1}0\} = \{2\bar{1}\bar{1}0\}$  left form of same. Each 3 faces.
- $\{pqr\}$  (where  $p+q+r=0\} = \{h\bar{k}0\}$  Right ditrigonal prism;  $\{prq\}$  (same values)  $= \{k\bar{i}\bar{h}0\}$  left ditrigonal prism. Each 6 faces.
- $\{pqq\}$  (two indices always equal)  $= \{h0\bar{h}l\}$  Positive or direct rhombohedron of the first order, including the primary one  $\{100\} = \{10\bar{1}1\}$ ;  $\{p'q'q'\}$  (where  $\begin{cases} p' = -p+4q \\ q' = 2p+q \end{cases}$ )  $= \{h0hl\}$  negative or inverse rhombohedron of the first order, including the complementary-primary inverse one  $\{\bar{1}22\} = \{\bar{1}011\}$ . Each 6 faces.
- $\{pqr\}$  (where one index = mean of other two)  $= \{h.h.\bar{2}h.l\}$  Right trigonal bipyramid of the second order;  $\{prq\}$  (same values)  $= \{2h.\bar{h}.\bar{h}.l\}$  left form of same. Each 6 faces.
- $\{pqr\} = \{h\bar{k}l\}$  Right positive trigonal trapezohedron;  $\{prq\}$  (same values)  $= \{k\bar{i}\bar{h}l\}$  left positive form of same;  $\{p'q'r'\}$  (where  $\begin{cases} p' = -p+2q+2r \\ q' = 2p-q+2r \\ r' = 2p+2q-r \end{cases}$ )  $= \{h\bar{k}l\}$  right negative form;  $\{p'r'q'\}$  (same values)  $= \{k\bar{i}hl\}$  left negative form. Each 6 faces.

By far the most important substance crystallising in this class is the universally distributed mineral quartz,<sup>1</sup> the common crystallised form of silica,  $\text{SiO}_2$ . The two varieties, right- and left-handed, of this mineral, frequently called rock crystal, afford excellent examples of opposite optical activity; the former rotates the plane of polarisation of a plane-polarised beam of light travelling along the trigonal axis, to the right (in the same sense as the morphology), and the latter rotates it to the left. They are consequently very largely employed in experiments on optical rotation and the circular polarisation of light. The two enantiomorphous varieties, moreover, are both found in large quantity in nature, and the absence of any well-defined cleavage, together with the beautifully clear transparency of the mineral, render it peculiarly valuable in optical work. A typical enantiomorphous pair of quartz crystals are represented in Figs. 311 and 312, the former being a left-handed crystal and the latter a right-handed one. Both varieties exhibit usually the hexagonal prism  $m = \{2\bar{1}\bar{1}\}$  and the primary direct and complementary primary inverse rhombohedra  $r = \{100\}$  and  $r' = \{\bar{1}22\}$ . The two rhombohedra are often so equally developed as to resemble a truly hexagonal terminal pyramid at each end of the prism. But in quartz crystals from certain particular localities, such as Schemnitz in Hungary, three faces of one rhombohedron largely predominate at each end, and crystals of quartz have also been found near Bristol as simple rhombohedra resembling cubes, for the rhombohedron angle is  $85^\circ 46'$ . But the fact that the symmetry is trapezohedral of class 18 is amply proved by the characteristic presence on optically right-handed crystals of more or less small faces of the right trigonal pyramid of the second order  $s = \{4\bar{1}\bar{2}\}$ , and of the right positive trapezohedron  $x = \{4\bar{1}\bar{2}\}$ , which give a distinctly right-handed appearance to the crystal, as is clearly shown in Fig. 312; and by the presence on optically left-handed crystals of

<sup>1</sup> For the structure of quartz as revealed by X-rays see Chapter XXXIII.



the complementary enantiomorphous left trigonal pyramid of the second order  $s = \{4\bar{2}1\}$  and of the left positive trigonal trapezohedron  $x = \{4\bar{2}\bar{1}\}$ , which endow the crystal morphologically also with a left-handed appearance, as illustrated in Fig. 311. It is usually possible to distinguish at once a crystal of quartz as a right-handed or a left-handed one by the presence of one or both of these forms, the two varieties of each or either of which never occur together on the same crystal, unless the latter be a twin and not a single individual. Moreover, when the  $x$ -face is absent,

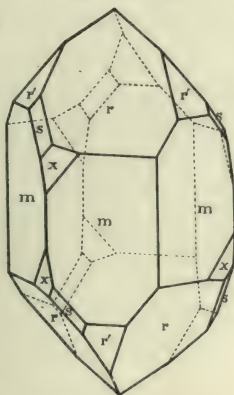


Fig. 311.—Left-Handed Crystal of Quartz.

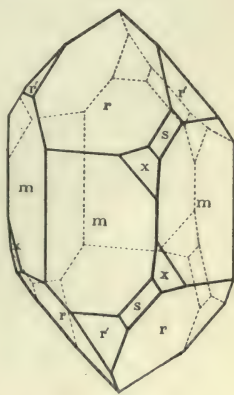


Fig. 312.—Right-Handed Crystal of Quartz.

and the rhombohedral faces are badly formed and untrustworthy, it often happens that a good little  $s$ -face (the trigonal pyramid) is present, and it almost invariably exhibits striæ which are parallel to the edge  $sr$ , the edge of intersection of the primary rhombohedron and the trigonal pyramid, and these striæ consequently at once locate the position of both faces and of the zones  $[r'sxm]$ , to the direction or zone-plane of which the striæ are parallel, and of the zone  $[rsm]$ , to the axis of which they are parallel but to the direction or zone-plane of which they are transverse. The  $s$ -faces lie at the intersection of these two zones. As regards surface markings, moreover, the faces of the direct rhombohedron  $r$  are generally brilliantly reflective, while those of the inverse rhombohedron  $r'$  are dull, affording much poorer reflections of the goniometer signal.

The holoaxial symmetry of class 18 is strikingly brought out on quartz crystals both by the figures obtained on the faces by etching with hydrofluoric acid, and by the pyro-electric phenomena displayed. The etched figures obtained on right-handed and left-handed crystals respectively are always oppositely enantiomorphous, that is, they are the mirror-images of each other. The figures on alternate faces of both the prism and the rhombohedra are characteristically different, exhibiting clearly the trigonal and not hexagonal nature of the symmetry. This will be apparent from Figs. 313 and 314. As regards the pyro-electric phenomena, any two opposite edges of the prism  $m = \{2\bar{1}\bar{1}\}$  are oppositely pyro-electric, so that when a section-plate of the hexagonal prism, parallel to the basal pinakoid, is heated and the Kundt mixture of powdered sulphur and red lead, usually employed in pyro-electric tests, is scattered over it, the negatively electrified sulphur is attracted to three alternate corners of the hexagonal plate as the latter cools, showing that the ends of the three digonal axes which emerge at these corners become positively

electrified by the molecular movements occurring during cooling; while the positively electrified red lead accumulates at the other three corners, the three other ends of the digonal axes, which in this case are those corresponding to the prism edges carrying the  $s$  and  $x$  faces, showing that

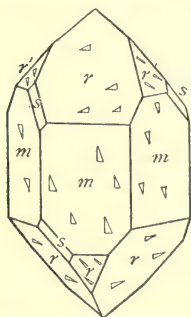


FIG. 313.—Etched Figures on Left-Handed Quartz Crystal.

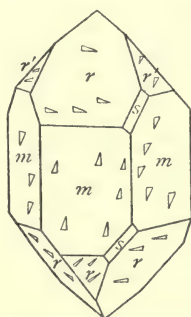


FIG. 314.—Etched Figures on Right-Handed Quartz Crystal.

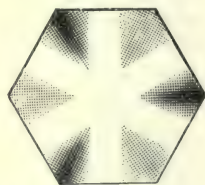


FIG. 315.—Distribution of Sulphur and Red Lead on Electrified Plate of Right-Handed Quartz.

these ends of the digonal symmetry axes become negatively electrified. The effect is shown in Fig. 315, the lighter shading representing sulphur and the darker red lead. The pyro-electric poles are thus the digonal axes, and the investigation of a hexagonal section of a crystal, perpendicular to the trigonal vertical axis, by Kundt's method is an excellent mode of determining the right- or left-handed nature of a crystal the faces of which may not be good enough for goniometrical examination.

The morphology of quartz is so instructive and important that a crystal of this mineral will be worked through goniometrically in the next chapter, as an example of trigonal symmetry.

*Class 17.—Rhombohedral Class. Diopase Class. Rhombohedral Hexagonal-Tetartohedral Class. Type, Hexagonal Alternating.*

As already stated in the introduction to this chapter, class 17 forms a link between the truly hexagonal classes and those of definitely trigonal symmetry. It may be almost equally well described as characterised by an alternating axis of hexagonal symmetry, or by a trigonal axis and a centre of symmetry. The symmetry is, however, most strictly described as consisting of the presence of a trigonal axis which is also a hexagonal axis of compound (mirror-image) symmetry. Fig. 316 represents this in stereographic projection, together with the poles of the general form.

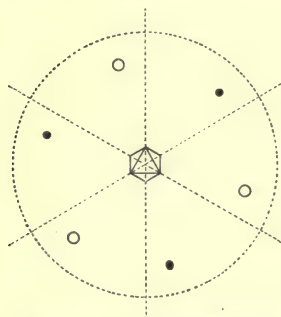


FIG. 316.—Symmetry Elements and General Form of Class 17.

This general form is one of those three (of classes 17, 18, and 19) already alluded to as consisting of an upper trigonal pyramid with a lower one below it, arranged

with respect to it either directly below (class 19) or rotated more or less about the trigonal axis. In the case of class 17, the operation of the hexagonal axis of compound symmetry causes the rotation to be exactly  $60^\circ$ , the reflection across the equatorial plane (not a plane of ordinary but only of reflective symmetry), immediately after the rotation, causing the three poles thus arranged at  $60^\circ$  on the projection, to those of the upper trigonal pyramid started with, to be in the lower hemisphere. It will be at once apparent that the arrangement of poles thus brought about is similar to that of the calcite or quartz rhombohedron, the only difference being that the **rhombohedron** is here one of the **third order**, that is, its poles do not lie, as do those of the calcite or quartz rhombohedron, on crystallographic axial radii, but within the spherical triangles produced by those radii and their intercepts on the primitive circle. Such a third order rhombohedron is shown in Fig. 317, the edges no longer lying in the axial planes. The actual one drawn is the rhombohedron  $\{20\bar{1}\}$  of dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , the Bravais-Miller axial ratio of which is  $a : c = 1 : 0.8322$ , and the Millerian axial angle  $\alpha = 102^\circ 53'$ , the Millerian axes being shown in broken-and-dotted lines. The indices of the upper faces are  $(20\bar{1})$ ,  $(\bar{1}20)$ , and  $(0\bar{1}2)$ ; and of the lower faces  $(25\bar{4})$ ,  $(\bar{4}25)$ , and  $(5\bar{4}2)$ .



FIG. 317.  
Third Order  
Rhombohedron.

It will also be apparent that the rhombohedron the poles of which are shown in Fig. 316 is only one of four such rhombohedra, all, however, mutually convertible by rotation, having the same rhombohedral angle. For the upper poles with which we start may be either right (as in Fig. 316) of the positive axial radii, or left of them; and they may be also right or left of the negative radii. The symbols will be  $\{pqr\}$ ,  $\{prq\}$ ,  $\{p'q'r'\}$ , and  $\{p'r'q'\}$ , where  $p'$ ,  $q'$ , and  $r'$  have the usual inverse values, as definitely stated in the list of forms on the next page.

**Special Cases.**—This class is well named the rhombohedral class, for in the first two special cases, when the poles fall on the Millerian axial radii themselves, or on the Bravais-Miller axial radii, **rhomboheda** are also produced, of the **first and second orders** respectively.

(1) When the poles lie on the Millerian axial radii and two of the indices are consequently equal, the **rhombohedron of the first order** is produced, the same as the calcite or quartz rhombohedron. It is a **positive or direct** one if the poles occupy the positive radii, or a **negative or inverse** one when the negative radii are occupied.

(2) When the poles fall on the Bravais-Miller axial radii, and one index becomes equal to the mean of the other two, a **right** or a **left rhombohedron of the second order** is produced, mutually convertible by rotation, as indeed are all three orders of rhombohedra, and each kind of each order. No enantiomorphism is developed at all in this class.

Just as the pyramidal forms of this class are all rhombohedra, so also the prismatic forms with faces parallel to the vertical trigonal axis are all hexagonal prisms. This will be obvious from the two facts that the poles are now all projected on to the primitive circle, and that the hexagonal axis of compound symmetry acts as if it were a truly hexagonal axis with respect to poles on the primitive circle, as all the poles lie equally in the plane of reflection.

(3) When the general poles of the third order rhombohedron are projected out on to the primitive circle, the **hexagonal prism** produced is of the **third order** also.

(4) If the poles lie at the ends of the Millerian axial radii, that is, when the poles of the first order rhombohedron are projected out on to the primitive circle, the **hexagonal prism** produced is one of the **first order**.

(5) When the second order rhombohedron is projected on to the primitive circle, or in other words, if the poles lie at the ends of the Bravais-Miller axial radii, the **hexagonal prism** is one of the **second order**.



(6) By the reflective operation of the hexagonal axis of compound symmetry the **basal pinakoid**, formed when the poles are concentrated at the centre of the projection, has both its faces in the same form, so that it is truly here a pinakoid.

A complete list of the forms in this class follows :

*List of Forms in Class 17.*

$\{111\} = \{0001\}$  Basal pinakoid. 2 faces.

$\{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$  Hexagonal prism of the first order. 6 faces.

$\{10\bar{1}\} = \{11\bar{2}0\}$  Hexagonal prism of the second order. 6 faces.

$\{pqr\}$  (where  $p+q+r=0$ ) =  $\{h\bar{k}0\}$  Hexagonal prism of the third order. 6 faces.

$\{pqq\}$  (two indices always equal) =  $\{h0\bar{h}l\}$  Positive or direct rhombohedron of the first order, including the primary one  $\{100\} = \{10\bar{1}1\}$  ;

$\{p'q'q'\}$  (where  $\begin{cases} p' = -p+4q \\ q' = 2p+q \end{cases}$ ) =  $\{\bar{h}0hl\}$  negative or inverse rhombohedron of the first order, including the complementary-primary inverse one  $\{\bar{1}22\} = \{\bar{1}011\}$ . Each 6 faces.

$\{pqr\}$  where one index = mean of other two) =  $\{h . h . 2\bar{h} . l\}$  Right rhombohedron of the second order ;

$\{prq\}$  (same values) =  $\{2h . \bar{h} . \bar{h} . l\}$  left rhombohedron of the second order. Each 6 faces.

$\{pqr\} = \{h\bar{k}l\}$  Right positive rhombohedron of the third order ;

$\{prq\} = \{k\bar{i}\bar{l}\}$  left positive rhombohedron of the third order ;

$\{p'q'r'\}$  (where  $\begin{cases} p' = -p+2q+2r \\ q' = 2p-q+2r \\ r' = 2p+2q-r \end{cases}$ ) =  $\{\bar{h}ikl\}$  right negative rhombohedron of the third order ;

$\{p'r'q'\}$  (same values) =  $\{\bar{k}i\bar{h}l\}$  left negative rhombohedron of the third order. Each 6 faces.

A good example of class 17 symmetry is afforded by the emerald-like mineral diopside, acid silicate of copper,  $\text{H}_2\text{CuSiO}_4$ , which has given its name to the class. Fig. 318 represents a crystal of diopside, the predominating prism faces  $a$  being those of the second order hexagonal prism  $\{10\bar{1}\}$  ; the rhombohedron  $r$  is the negative or inverse rhombohedron  $\{11\bar{1}\}$ , and  $s$  is the third order rhombohedron  $\{7\bar{7}6\}$ . The presence of this latter form indicates the class conclusively. The mineral cleaves admirably parallel to the faces of the possible primary rhombohedron  $\{100\}$ , which latter form, however, is rarely developed in natural faces. The beautiful shimmer which the green and not perfectly transparent crystals exhibit is due to internal reflections from the cleavage cracks of  $\{100\}$ . According to Breithaupt the Bravais-Miller axial ratio  $a:c=1:0.5342$ . The Millerian axial angle  $\alpha=111^\circ 42'$ .

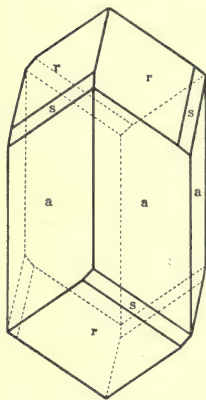


FIG. 318.  
Crystal of Diopside.

*Class 16.—Trigonal Pyramidal Class. Hemimorphic Tetartohedral Class. Type, Trigonal Polar.*

We now come to the last of the 32 classes of symmetry, and the seventh and last class of the trigonal system. It is characterised by the minimum of symmetry essential to that system, namely, a trigonal axis of symmetry only. It has been shown in the introduction to this chapter that the simple general form produced is a single (upper or lower) trigonal (three-faced) pyramid, as shown in the stereographic projection Fig. 319, which gives the poles of the upper pyramid.

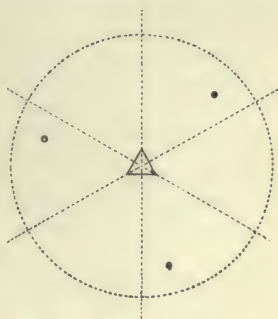


FIG. 319.—Symmetry Element and General Form of Class 16.

The form in either case is a **trigonal pyramid of the third order**. There are, however, four such upper pyramids possible, the poles of which are respectively right and left of either the positive or negative Millerian axial radii. The one shown in Fig.

319 is the **upper right positive form**  $\{pqr\} = \{hikl\}$ . The **upper left positive form** is  $\{prq\} = \{k\bar{i}hl\}$ , the Millerian index numbers of the right form being interchanged without any change of sign; its poles are as far on the left side of the positive radii as the right form poles were on the right. Similarly the two upper forms with poles equally far from the negative radii are called the **upper right negative trigonal pyramid**  $\{p'q'r'\} = \{\bar{h}ikl\}$ , and the **upper left negative form**  $\{p'r'q'\} = \{\bar{k}i\bar{h}l\}$ , where the values  $p'$ ,  $q'$ , and  $r'$  bear the relation to the values  $p$ ,  $q$ , and  $r$  which has been shown to be the general relation of the indices of an inverse face to that of a direct face, namely,

$$p' = -p + 2q + 2r, \quad q' = 2p - q + 2r, \quad r' = 2p + 2q - r.$$

Besides these four upper trigonal pyramids, there are four analogous lower pyramids, the symbols of which (both Millerian and Bravais-Millerian) are the same as those of the upper pyramids, but with all the signs changed, the convention being that the lower right positive form is that one the faces of which are parallel to those of the upper right positive, and so on, the terms being similar as regards right or left, positive or negative, for such pairs of upper and lower forms as are parallel.

Hence there are no less than eight separate open forms, each consisting of three faces meeting pyramidally in a common apex, in the general case of class 16.

**Special Cases.**—(1) When two of the indices are equal, and the poles fall on the Millerian axial radii in the projection, the **trigonal pyramid** becomes one of the **first order**, and there can be four such, a **positive** and a **negative upper form**, according as the three poles occupy the positive or the negative radii, and two analogous lower forms parallel to the upper ones. It is a particular **upper positive primary trigonal pyramid** the faces of which are chosen for the Millerian axial planes, and its edges for the directions of the axes. Its symbol is, of course,  $\{100\}$ , and its poles generally occupy positions not far removed from half-way between the centre and the primitive circle. The form in general is usually expressed by the symbol  $\{pqq\}$ , as two of the indices are always equal. Considering the particular faces the poles of which fall on the back-and-front diameter, one of which is  $(100)$ , and the indices of which are taken for the form symbols, those between the primary face  $(100)$  and the basal plane  $(111)$  are of the nature  $(pqq)$ , as regards the signs of the indices, while those between  $(100)$

and the prism face ( $2\bar{1}\bar{1}$ ) are of the type ( $p\bar{q}\bar{r}$ ). This will be clear from Fig. 285. An important negative form is  $\{011\}$ , the faces of which replace the edges of the primary pyramid  $\{100\}$ , each face lying in the same zone with two adjacent faces of the latter form.

(2) When the poles of the trigonal pyramid occupy the Bravais-Miller axial radii intermediate between the Millerian, one of four possible **trigonal pyramids of the second order** is produced, which is distinguished as **upper right** when the right front sextant of the projection is occupied by one of the three poles in the upper hemisphere, or **upper left** when the left sextant is so occupied, and as **lower right** or **lower left** when the faces are in the lower hemisphere and parallel to the directions of the faces of the two upper forms. The symbols of these four second order trigonal pyramids are given in the list of forms.

(3) When the poles migrate on to the primitive circle, in general a **trigonal prism of the third order** parallel to the vertical trigonal axis is produced. There are four such prismatic forms possible, each corresponding to the limiting case of a pair of third order pyramids, namely, a **right positive** and **left positive**, with poles on the right or the left of the positive radii respectively, and a **right negative** and **left negative**, with poles to right or left of the three negative radii. Their symbols are given in the list below.

(4) When the poles move along the primitive circle until they fall on the ends of the Millerian axial radii, the four forms are reduced to two, a **positive** and a **negative trigonal prism of the first order** respectively, according as the positive or the negative ends are occupied. The positive form is  $\{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$  and the negative form  $\{211\} = \{\bar{1}010\}$ . They are the limiting cases of pairs of pyramids of the first order.

(5) When the movement is on to the ends of the Bravais-Miller axial radii the **trigonal prism is of the second order**, and may be the **right**  $\{10\bar{1}\} = \{11\bar{2}0\}$  or the **left**  $\{\bar{1}10\} = \{2\bar{1}\bar{1}0\}$  of the two possible forms of the same, which are the limiting cases of pairs of second order pyramids.

(6) The **basal plane**, the limiting form of all trigonal pyramids,—when the poles concentrate and coalesce in the centre of the projection, the inner corner of each segmental triangle,—is divided into two separate forms, the **upper basal plane** or **pedion**  $\{111\} = \{0001\}$ , and the **lower basal plane** or **pedion**  $\{\bar{1}\bar{1}\bar{1}\} = \{000\bar{1}\}$ .

The following list gives the symbols of all these forms :

*List of Forms in Class 16.*

$\{111\} = \{0001\}$  Upper basal plane or pedion ;  $\{\bar{1}\bar{1}\bar{1}\} = \{000\bar{1}\}$  lower basal plane or pedion. Each 1 face.

$\{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$  Positive trigonal prism of the first order ;

$\{211\} = \{\bar{1}010\}$  negative form of same. Each 3 faces.

$\{10\bar{1}\} = \{11\bar{2}0\}$  Right trigonal prism of the second order ;

$\{\bar{1}10\} = \{2\bar{1}\bar{1}0\}$  left form of same. Each 3 faces.

$\{pqr\}$  (where  $p+q+r=0$ ) =  $\{h\bar{k}0\}$  Right positive trigonal prism of the third order ;  $\{prq\} = \{k\bar{i}h0\}$  left positive form of same ;

$\{p'q'r'\}$  (where  $\begin{cases} p' = -p+2q+2r \\ q' = 2p-q+2r \\ r' = 2p+2q-r \end{cases}$ ) =  $\{\bar{h}ik0\}$  right negative form ;

$\{p'r'q'\} = \{\bar{k}i\bar{h}0\}$  left negative form. Each 3 faces.

$\{pqq\}$  (where two indices are always equal) =  $\{h0\bar{h}l\}$  Upper positive trigonal pyramid of the first order ; including the primary form  $\{100\} = \{10\bar{1}\bar{1}\}$  ;

$\{p'q'q'\}$  (where  $\begin{cases} p' = -p+4q \\ q' = 2p+q \end{cases}$ ) =  $\{\bar{h}0hl\}$  upper negative form ;

$\{\bar{p}\bar{q}\bar{q}\} = \{\bar{h}0h\bar{l}\}$  lower positive form, parallel to upper positive ;



$\{\bar{p}'\bar{q}'\bar{r}'\} = \{h0\bar{h}\bar{l}\}$  lower negative form, parallel to upper negative. Each 3 faces.

$\{pqr\}$  (where one index = mean of other two) =  $\{h . h . 2\bar{h} . l\}$  Upper right trigonal pyramid of the second order ;

$\{prq\}$  (same values) =  $\{2h . \bar{h} . \bar{h} . l\}$  upper left form of same ;

$\{\bar{p}\bar{q}\bar{r}\} = \{\bar{h} . \bar{h} . 2h . l\}$  lower right form, parallel to upper right form ;

$\{\bar{p}\bar{r}\bar{q}\} = \{2\bar{h} . h . h . \bar{l}\}$  lower left form, parallel to upper left form. Each 3 faces.

$\{pqr\} = \{h\bar{h}i\bar{l}\}$  Upper right positive trigonal pyramid of the third order ;

$\{prq\} = \{k\bar{i}h\bar{l}\}$  upper left positive form of same ;

$\{p'q'r'\}$  (where  $\begin{cases} p' = -p + 2q + 2r \\ q' = 2p - q + 2r \\ r' = 2p + 2q - r \end{cases}$ ) =  $\{h\bar{i}k\bar{l}\}$  upper right negative form ;

$\{p'r'q'\} = \{\bar{k}i\bar{h}\bar{l}\}$  upper left negative form ;

$\{\bar{p}\bar{q}\bar{r}\} = \{h\bar{i}k\bar{l}\}$  lower right positive form ;

$\{\bar{p}\bar{r}\bar{q}\} = \{\bar{k}i\bar{h}\bar{l}\}$  lower left positive form ;

$\{\bar{p}'\bar{q}'\bar{r}'\} = \{h\bar{i}k\bar{l}\}$  lower right negative form ;

$\{\bar{p}'\bar{r}'\bar{q}'\} = \{\bar{k}i\bar{h}\bar{l}\}$  lower left negative form. Each 3 faces.

The best example of this class of symmetry is afforded by sodium periodate,  $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ , a crystal of which is represented in Fig. 320. It exhibits predominatingly the primary upper positive trigonal pyramid of the first order  $r = \{100\}$  and the lower basal plane  $c = \{\bar{1}\bar{1}\bar{1}\}$ , also an upper negative trigonal pyramid of the first order  $e = \{11\bar{1}\}$  in fair-sized faces, and as a subsidiary but very important form (as indicating the class)  $s = \{201\}$  an upper left trigonal pyramid of the second order, the faces of which occur as narrow and oblique replacements of the edges of the primary predominating first order pyramid  $\{100\}$ . These latter edges are sometimes replaced instead, however, by symmetrical (not oblique) strips of the upper negative first order pyramid  $\{011\}$ , in which case still narrower strips of the third order right negative trigonal pyramid  $\{504\}$  accompany them on one side only, thus proving conclusively that the symmetry is that of class 16. Such crystals rotate the plane of polarisation to the left. Other crystals show more or less of these forms, but with strips of the left negative trigonal pyramid of the third order developed instead of those of the right negative form, and are thus enantiomorphous to the first kind ; these rotate the plane of polarisation to the right. This substance thus shows unmistakably the enantiomorphism of class 16, and the opposite optical activity corresponding thereto. The Bravais-Miller ratio of the axes is  $a : c = 1 : 1.094$ , and the Millerian axial angle  $\alpha = 94^\circ 9'$ .

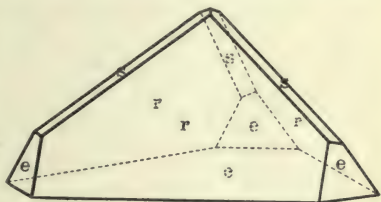


FIG. 320.—Crystal of Sodium Periodate.

## CHAPTER XXIII

### TWO PRACTICAL EXAMPLES OF TRIGONAL CRYSTALS, QUARTZ AND CALCITE

#### (1) *Example of Class 18. Quartz, $\text{SiO}_2$ .*

THIS first example of a trigonal crystal is a particularly well formed left-handed crystal of quartz, about a centimetre long in the direction of the prism and half a centimetre thick across the prism. It is only singly terminated the other end having been attached to the cavity wall in which it had grown. It forms an excellent example of class 18 symmetry, and also shows the characteristics of this exceptionally interesting and important mineral very clearly, as described and illustrated on pages 354 to 356 in the last chapter, particularly as regards the development of those faces which determine its right- or left-handedness.

As usual, a careful freehand drawing was made of the crystal. The decision as to the correct mode of arranging it offered no difficulty in this case, as the disposition of the faces was obviously that of the usual first order hexagonal prism of quartz  $m = \{2\bar{1}1\} = \{10\bar{1}0\}$ , terminated by the complementary-primary direct and inverse rhombohedra  $r = \{100\} = \{10\bar{1}1\}$  and  $r' = \{122\} = \{\bar{1}011\}$ . The cleavage directions of quartz are parallel to the faces of the primary rhombohedron  $r = \{100\}$ , but the cleavage is a very imperfect one, and no trace of it was visible on the crystal in question.

There were also two brilliant small faces present which appeared to be those of the forms  $s = \{4\bar{2}1\} = \{2\bar{1}\bar{1}1\}$  and  $x = \{4\bar{2}\bar{1}\} = \{6\bar{1}\bar{5}1\}$ , the left trigonal pyramid of the second order and the left positive trapezohedron; the two actual faces were apparently those the indices of which are the same as the two form symbols just quoted, and were clearly indicative of the left-handed nature of the crystal. Another pair of these small faces were also present, although not so well developed as the first pair; the third pair, possible from the nature of trigonal symmetry, were absent. The freehand drawing was subsequently, after the completion of the measurements and consequent verification of the nature of the faces, elaborated into the correct representation to scale reproduced in Fig. 321, in accordance with the usual convention which ensures that

lines actually parallel on the crystal shall remain so in the drawing. The actual construction for this quartz crystal will be found described in Chapter XXV., page 419.

Obviously the first measurements to make were those of the angles in the prism zone. The crystal was therefore adjusted on the goniometer with the vertical axis, the axis of the prism, parallel to that of the goniometer, and the zone measured. Five of the six faces gave excellent single reflections of the signal-slit, and are accordingly marked with the letter A. The following results were obtained :

## Prism Zone Readings.

$m$	$335^{\circ} 16' A$
$m$	$275 \quad 8$
$m$	$215 \quad 15 A$
$m$	$155 \quad 18 A$
$m$	$95 \quad 17 A$
$m$	$35 \quad 16 A$
$m$	$335 \quad 16 A$

## Interfacial Angles.

$mm$	$60^{\circ} 8'$
$mm$	$59 \quad 53$
$mm$	$59 \quad 57 A \text{ value}$
$mm$	$60 \quad 1 A \quad "$
$mm$	$60 \quad 1 A \quad "$
$mm$	$60 \quad 0 A \quad "$

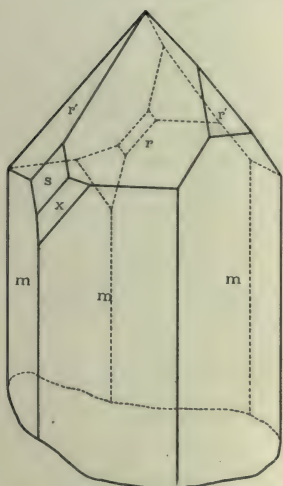


FIG. 321.—The Measured Crystal of Quartz.

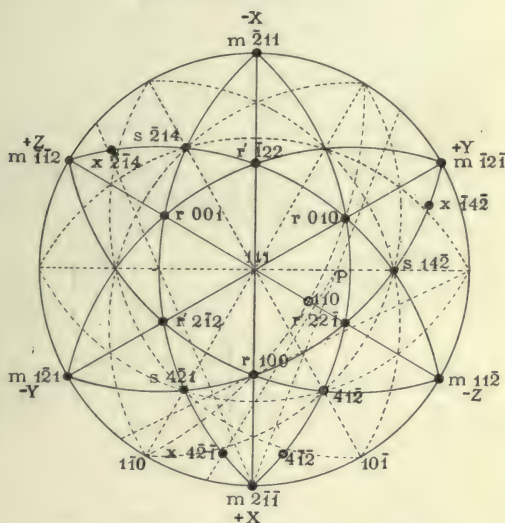


FIG. 322.—Stereographic Projection of Quartz.

It will be clear that the true values of all these six angles between successive faces of the prism zone are intended to be  $60^{\circ}$ , the four "A" values, each afforded by a pair of perfect faces yielding irreproachable "A" images, being within  $3'$  of  $60^{\circ} 0'$ , that is, within the usual limits of error observed with excellent faces. It would be useless here, and if the symmetry of quartz were not so thoroughly established it might be very misleading, to take the arithmetical mean of the six values of the prism angle. For, as they together make up  $360^{\circ}$  the mean is bound to be  $60^{\circ} 0'$ , whereas it might have been possible that a pseudo-hexagonal crystal of orthorhombic symmetry were under investigation, with 3 angles of nearly but not quite  $60^{\circ}$  in each semicircle, and the mean here could have afforded us no information at all, and even worse, it would have caused us incorrectly to attribute real hexagonal symmetry to the crystal.



The prism is, however, in the case of quartz a truly hexagonal one, but the proof lies in the practical identity of adjacent "A" values of the angle, and not in any mean value. The six poles lie on the primitive circle of the stereographic projection, which we can now begin to construct, and which is shown in Fig. 322.

The next measurement in importance is that between any prism face and a face of either rhombohedron, that is, the determination of the angles  $mr$  and  $mr'$ . They belong to three similar zones, represented in the projection by the three diameters  $mrr'm$ , obtained by drawing straight lines to join opposite poles on the primitive circle, representing parallel prism faces, such straight lines obviously passing through the centre of the circle. For, on adjusting parallel to the goniometer axis the edge between one of the prism faces and the rhombohedral end face situated immediately above it, say the one marked  $r$  in Fig. 321, measuring the angle between these two faces, which are represented in the projection, Fig. 322, by the poles  $m=(2\bar{1}\bar{1})$  and  $r=(100)$  on the front half of the diameter running vertically in the page, and then continuing to rotate the crystal on the goniometer, two other faces were found in the zone, namely, another rhombohedral face  $r'=(\bar{1}22)$  in the projection, and  $m=(\bar{2}11)$  the prism face parallel to the one started with. The  $r$  and  $r'$  faces were those of the direct and inverse rhombohedra. The angle between these two further faces in the zone proved to be the same as that between the first two faces, so that the angles  $mr=(2\bar{1}\bar{1}): (100)$  and  $mr'=(\bar{2}11): (122)$  appeared to be identical. Before being certain, however, it was necessary to measure also the two other similar zones, represented by the other two diameters. For according to trigonal symmetry these three zones, the planes of which (projected in the diameters) contain the Millerian crystallographic axes, should be exactly similar. The actual measurements derived from all three zones are appended.

Circle Readings.	Angles.	Circle Readings.	Angles.	Circle Readings.	Angles.
$\left\{ \begin{array}{l} m \ 225^\circ \ 10' \\ r \ 186 \ 54 \\ r' \ 83 \ 26 \ A \\ m \ 45 \ 10 \ A \end{array} \right.$	$\left\{ \begin{array}{l} mr \ 38^\circ \ 16' \\ rr' \ 103 \ 28 \\ r'm \ 38 \ 16 \ A \end{array} \right.$	$\left\{ \begin{array}{l} m \ 239^\circ \ 24' \\ r' \ 201 \ 9 \\ r \ 97 \ 37 \ A \\ m \ 59 \ 24 \ A \end{array} \right.$	$\left\{ \begin{array}{l} mr' \ 38^\circ \ 15' \\ r'r \ 103 \ 32 \\ rm \ 38 \ 13 \ A \end{array} \right.$	$\left\{ \begin{array}{l} m \ 226^\circ \ 44' \\ r \ 188 \ 33 \\ r' \ 84 \ 54 \ A \\ m \ 46 \ 44 \ A \end{array} \right.$	$\left\{ \begin{array}{l} mr \ 38^\circ \ 11' \\ rr' \ 103 \ 39 \\ r'm \ 38 \ 10 \ A \end{array} \right.$

It will be clearly apparent that the three values of  $mr$  and the three of  $mr'$  are all six so nearly equal that it can be safely accepted that the true values of  $mr$  and  $mr'$  are identical, the differences from equality being only such as are quite accounted for by the varying nature of the reflected signal-images.

The mean of the three values of  $mr$  is  $38^\circ 13'$ , and that of the three values of  $mr'$  is  $38^\circ 14'$ . The single A-value of  $mr$  is  $38^\circ 13'$ , and the mean of the two A-values of  $mr'$  is also  $38^\circ 13'$ . Hence there is no doubt that the real value of both angles is  $38^\circ 13'$ . This value is identical with that generally accepted for this angle on quartz crystals (Miers' *Mineralogy*, p. 367). Now the knowledge of this one angle suffices to enable us to calculate all the other angles between the crystal faces, one known basal angle only being required for hexagonal, trigonal, or tetragonal crystals, as explained in Chapter VII. This angle  $mr$  is a very convenient one to choose as basal angle, for it forms one of the elements of a right-angled spherical triangle,  $m=(2\bar{1}\bar{1})$ ,  $r=(100)$ ,  $m=(11\bar{2})$ , the side  $mm$  of which is also known, being  $60^\circ$  by reason of the symmetry, a fact confirmed by

the measurement of the prism zone. Hence we shall be able to use the simple Napierian rules for right-angled triangles in commencing the calculations.

We can now insert the six poles  $r$  and  $r'$  in their proper places on the three diameters of the projection, Fig. 322. It is only necessary to find the position of one of them by the proper construction, given on page 66 in Chapter IV., and then to mark off with the compasses similar distances from the centre in the cases of the other five. Constructing for the  $r$  face (100), we set off with the protractor an arc of  $38^{\circ} 13'$  from  $m$ , the extremity of the diameter, along the primitive circle, say to the left, and join this point thus set off to the pole of the zone circle represented by the diameter, such pole being at the right end of the horizontal dotted diameter at right angles to that on which  $r=(100)$  is situated. This junction line passes through the pole  $r=(100)$ , intersecting the diameter at it.

There are six other important zones to be measured, namely, the six represented by the circular arcs ending at the  $m$ -faces in the projection, which have been constructed to pass through an  $r$  and an  $r'$  face in each case. One of these zones is the very important one most obviously inviting measurement, in which occur the small faces  $s$  and  $x$  determinative of the right- or left-handed nature of the crystal. This zone consists of the front prism face  $m$ , then the trapezohedral face  $x$ , next the trigonal pyramid face  $s$ , then the inverse rhombohedral face  $r'$ ; we afterwards come to the faces which are behind in the drawing, Fig. 321, namely, the direct rhombohedral face  $r$ , the small second face of the trigonal pyramid  $s$ , and finally in completion of the zone the prism face  $m$  parallel to the one started with. The measurements obtained with this zone are set forth below :

Circle Readings.	Angles.
$\left\{ \begin{array}{l} m \ 289^{\circ} \ 25' \\ x \ 277 \ 24 \\ s \ 251 \ 30 \ A \\ r' \ 222 \ 35 \ A \\ r \ 176 \ 18 \ A \\ s \ 147 \ 30 \\ m \ 109 \ 31 \end{array} \right.$	$\left. \begin{array}{l} mx \ 12^{\circ} \ 1' \\ xs \ 25 \ 54 \\ sr' \ 28 \ 55 \ A \\ r'r \ 46 \ 17 \ A \\ rs \ 28 \ 48 \\ sm \ 37 \ 59 \end{array} \right\} \begin{array}{l} ms \ 37^{\circ} \ 55' \\ mr' \ 66^{\circ} \ 50' \\ rm \ 66 \ 47 \end{array}$

The six zones, of which this is the most completely developed on the crystal before us, may be subdivided into two sets of three each, namely, three on which the poles  $s$  and  $x$  occur, and three on which they do not occur. As already stated, two faces corresponding to each of these  $s$  and  $x$  forms were actually developed on the crystal, the third face, however, in each case being absent. Both the  $s$  faces were on the zone just measured, and gave trustworthy reflections, one affording an "A" image. Each of them also occurred on another of the three zones (a separate zone in each case) just referred to, at its intersection with the zone just measured, and these two further zones were next measured and gave the values set out on the next page. The second  $x$ -face was

present on one of them, but the reflection was not sufficiently good to afford a trustworthy value, although adequate to enable one to identify the face as belonging to the form  $x$ .

The fact of the  $s$ -poles being thus situated at the intersection of two of these zones indicated by the circular arcs defines their positions on the stereographic projection without any further construction. It also enables us to determine the indices of the form  $s$ , by cross-multiplication of the two zone symbols, and thus to verify that the symbol is  $\{4\bar{2}1\}$ .

Let us verify the indices of the pole  $(4\bar{2}1)$  on the left of the radius  $(2\bar{1}\bar{1}) : (111)$ . It is on the zones  $(2\bar{1}\bar{1}) : (2\bar{1}2)$  and  $(1\bar{2}1) : (100)$ , and of these we find the zone symbols and cross-multiply.

$$\begin{array}{rcl} 2\bar{1}\bar{1}2\bar{1}\bar{1} & & 1\bar{2}11\bar{2}1 \\ \times \times \times & = [360] = [120]; & \times \times \times = [012]; \\ 2\bar{1}2\bar{2}\bar{1}2 & & 100100 \end{array}$$

$$\begin{array}{rcl} 120120 & & \\ \times \times \times & = (4\bar{2}1). & \\ 012012 & & \end{array}$$

Hence  $(4\bar{2}1)$  is in fact the correct symbol.

In order to locate the position of the facial pole  $x$  on the projection, the pole of the arc  $m x s r m$  is first found on the dotted horizontal diameter, by the construction of page 97, Chapter VI. A straight line is first drawn from  $m = (2\bar{1}\bar{1})$  to the left upper part of the primitive circle, passing through the intersection of the arc and the horizontal diameter. An arc of  $90^\circ$  is then marked off on the primitive circle, and the point thus found on the right upper part of the primitive circle is joined to  $m = (2\bar{1}\bar{1})$ . Where it cuts the horizontal diameter is the pole  $P$  of the arc. To find the facial pole  $x$  we then set off  $12^\circ$ , the measured angle from  $m = (2\bar{1}\bar{1})$ , to the left along the primitive circle, and join the point thus obtained to  $P$ , the pole of the arc. Where this line cuts the arc is the facial pole  $x$ . These constructions are shown in Fig. 322.

Circle Readings.	Angles.	Circle Readings.	Angles.
$\left\{ \begin{array}{l} m \ 297^\circ \ 5' \\ r' \ 230 \ 11 \text{ A} \\ r \ 184 \ 0 \text{ A} \\ s \ 154 \ 55 \text{ A} \\ m \ 117 \ 5 \end{array} \right.$	$\left. \begin{array}{l} mr' \ 66^\circ \ 54' \\ r'r \ 46 \ 11 \text{ A} \\ rs \ 29 \ 5 \text{ A} \\ sm \ 37 \ 50 \end{array} \right\} rm \ 66^\circ \ 55'$	$\left\{ \begin{array}{l} m \ 344^\circ \ 43' \\ s \ 306 \ 46 \text{ A} \\ r' \ 277 \ 42 \text{ A} \\ r \ 231 \ 32 \\ m \ 164 \ 43 \end{array} \right.$	$\left. \begin{array}{l} ms \ 37^\circ \ 57' \\ sr' \ 29 \ 4 \text{ A} \\ r'r \ 46 \ 10 \\ rm \ 66 \ 49 \end{array} \right\} mr' \ 67^\circ \ 1'$

In addition to these complete zone measurements, two further good values of  $mr$  were obtained, namely,  $66^\circ 45' \text{ A}$  and  $66^\circ 40'$ , and one value of  $rr'$ ,  $46^\circ 35'$ , from the other three similar zones on which the  $s$  and  $x$  faces do not occur, the reflections from other faces in these zones not being adequately trustworthy.

The various values of the same angle obtained from these six similar zones were collected and the following mean values extracted :

$$mx = 12^\circ 1', xs = 25^\circ 54', ms = 37^\circ 55', sr \text{ or } sr' = 28^\circ 58', mr \text{ or } mr' = 66^\circ 50', rr' = 46^\circ 18'.$$

This completes the angular measurements necessary for the perfect demonstration of the symmetry of the crystal, and for the determination of the elements.

We are now, therefore, in a position to proceed to the calculation



of these six angles, from the basal angle  $mr = (2\bar{1}\bar{1}) : (100) = 38^\circ 13'$ , in order to confirm the measured values thus arrived at; and after this is done we shall be able to compile our final table of angles and to calculate the elements.

### Calculation of Angles and Elements.

The basal angle  $mr = (2\bar{1}\bar{1}) : (100) = 38^\circ 13'$ , forms one of two known sides, the other being  $mm = 60^\circ$ , in the right-angled triangle  $mmr$  ( $2\bar{1}\bar{1}$ ), ( $11\bar{2}$ ), ( $100$ ), already alluded to, and which will readily be recognised in the projection, Fig. 322.

We may conveniently begin the calculations by finding the third side of this triangle, namely  $rm = (100) : (11\bar{2})$ . Constructing the Napierian diagram we have, by Napier's rules :

$$\cos rm = \cos 60^\circ \cos 38^\circ 13'. \quad rm = 66^\circ 52'.$$

The mean measured value of  $rm$  was  $66^\circ 50'$ , a satisfactory agreement.

We may next conveniently pass to the calculation of the angle  $ms = (2\bar{1}\bar{1}) : (4\bar{2}1)$ . The first step is to calculate the angle at  $m$ , ( $11\bar{2}$ ), in the same triangle  $mmr$ . By Napier's rules :

$$\cos m = \tan 60^\circ \cot 66^\circ 52'. \quad m = 42^\circ 16'.$$

This angle, however, is the same as the angle at  $m$ , ( $2\bar{1}\bar{1}$ ), in the right-angled triangle  $m = (2\bar{1}\bar{1})$ ,  $s = (4\bar{2}1)$ , ( $1\bar{1}0$ ), by reason of the symmetry, and we also know a second side in this triangle, namely,  $m = (2\bar{1}\bar{1}) : (1\bar{1}0)$ , for it is obviously  $30^\circ$ , the pole ( $1\bar{1}0$ ) being at the end of one of the Bravais-Miller axes, and although the face corresponding to the pole is not developed we can, of course, utilise our knowledge of its position in the calculations, for it depends entirely on the symmetry, which we have proved to be trigonal. Constructing the Napierian diagram, and applying the rules :

$$\begin{aligned} \cos s &= \sin 42^\circ 16' \cos 30^\circ. & \cos ms &= \cot 42^\circ 16' \cot s. \\ s &= 54^\circ 22\frac{1}{2}'. & ms &= 37^\circ 58'. \end{aligned}$$

Or we might have calculated  $ms$  in one step from the equation  $\cos 42^\circ 16' = \tan 30^\circ \cot ms$ , for by transposition  $\cot ms = \cos 42^\circ 16' \cot 30^\circ$ . The value yielded for  $ms$  is the same, namely,  $37^\circ 58'$ .

The mean measured value of  $ms$  was  $37^\circ 55'$ .

Again, by reason of the symmetry, as the six zonal arcs are in pairs symmetrical to the diameters at the ends of which they intersect, and as the three pairs of such arcs are equal (as indeed are all six arcs), the value of  $rm$  obtained from the first triangle, namely  $66^\circ 52'$ , is the same as the value of  $mr' = (2\bar{1}\bar{1}) : (2\bar{1}2)$ . Hence, as we have now found the value of part of this angle, namely,  $ms$ , we can obtain the value of another angle required to be calculated,  $sr'$ , by difference. That is :

$$sr' = (4\bar{2}1) : (2\bar{1}2) = mr' - ms = 66^\circ 52' - 37^\circ 58' = 28^\circ 54'.$$

The mean measured value of  $sr'$  (or of  $sr$ ) was  $28^\circ 58'$ .

The remaining angle common to these six zones,  $rr'$ , is also at once afforded, for

$$rr' = (001) : (2\bar{1}2) = 180^\circ - 2mr = 180^\circ - 2(66^\circ 52') = 46^\circ 16'. \quad (\text{Measured } 46^\circ 18').$$

It only remains now to calculate the position of the trapezohedron face  $x$ . On constructing the stereographic projection from the mean measured angles, it was observed that the pole  $x$  of the trapezohedron face which gave a good reflection in the zone [ $m = (2\bar{1}\bar{1})$ ,  $r' = (2\bar{1}2)$ ] was not quite at the intersection of this zone with the other zone obtained by constructing a circular arc to pass through the ends of the Bravais-Miller diameter perpendicular to ( $1\bar{1}0$ ) and through the poles  $s = (14\bar{2})$  and ( $4\bar{1}2$ ). An angle of  $12^\circ 1'$  from  $m = (2\bar{1}\bar{1})$  places the pole  $x$  about  $2\frac{1}{2}^\circ$  nearer  $m$  than the intersection of the two zonal arcs. Now the well-known trapezohedral forms shown by quartz

crystals from all over the world, one pole of each of which lies in the zone  $[msr']$ , are  $u = \{8\bar{4}\bar{1}\}$ ,  $y = \{10 \cdot \bar{5} \cdot \bar{2}\}$ , and  $x = \{4\bar{2}\bar{1}\}$ , the last being the nearest to  $m = (2\bar{1}\bar{1})$  and the other two in consecutive order in the zone towards  $s = (4\bar{2}\bar{1})$ . If now we calculate the indices of the pole at the intersection of this zone with the zone  $[(1\bar{1}0) : (41\bar{2})]$ , by cross-multiplication, we get :

$$\begin{array}{rcl} 4 \bar{2} 1 & 4 \bar{2} 1 & \\ \times \times \times & = [360] = [120]; & 4 \bar{1} \bar{2} 4 1 \bar{2} \\ 2 \bar{1} \bar{1} 2 \bar{1} \bar{1} & & \times \times \times = [\bar{2}\bar{2}5] = [225]; \\ & & 1 \bar{1} 0 1 \bar{1} 0 \\ & 120120 & \\ & \times \times \times & \\ & 225225 & = (10 \cdot \bar{5} \cdot \bar{2}). \end{array}$$

Evidently the pole at the intersection is  $(10 \cdot \bar{5} \cdot \bar{2})$ , so that  $x$  cannot have these indices, not being at the intersection, but must be the next trapezohedron in order towards  $m = (2\bar{1}\bar{1})$ , namely,  $(4\bar{2}\bar{1})$ . Assuming these latter, therefore, to be the indices of the trapezohedral pole  $x$  which gave the good reflection, we can proceed to find its position in the zone  $[msr']$  by means of the anharmonic ratio of the four poles bearing these letters in the zone, for all their indices are known, and the angular positions of three of them with respect to each other are also known. Fig. 323 shows the data.

To find  $mx$  and  $xs$  :

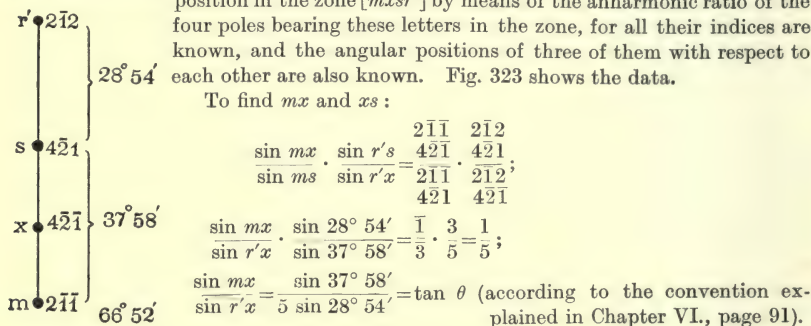


FIG. 323.

$$\theta = 14^\circ 17'.$$

Transforming now to the sum and difference of two tangents, as discussed in Chapter VI., we have :

$$\begin{aligned} \tan \frac{r'x - mx}{2} &= \tan \frac{66^\circ 52'}{2} \tan (45^\circ - 14^\circ 17') \\ &= \tan 33^\circ 26' \tan 30^\circ 43'. \end{aligned}$$

$$\frac{r'x - mx}{2} = 21^\circ 25'.$$

We thus find :

$$r'x - mx = 42^\circ 50',$$

and we know that :

$$r'x + mx = 66^\circ 52'.$$

Hence, adding :

$$2r'x = 109^\circ 42', \text{ and } r'x = 54^\circ 51';$$

and subtracting :

$$2mx = 24^\circ 2', \text{ and } mx = 12^\circ 1'.$$

We thus arrive at the angle  $12^\circ 1'$  for  $mx$ , a value identical with the single measured angle, a result which is thus very satisfactory, and definitely decides that the indices of  $x$  are  $(4\bar{2}\bar{1})$ .

The last angle remaining to calculate,  $xs$ , can be got by difference from  $ms$ , and is :

$$xs = ms - mx = 37^\circ 58' - 12^\circ 1' = 25^\circ 57'. \text{ (Measured } 25^\circ 54'.)$$

It may perhaps be worth while to confirm the assumption that  $x$  cannot be  $(10 \cdot \bar{5} \cdot \bar{2})$ , by actually calculating the position of  $x$  on the assumption of these indices instead of  $(4\bar{2}\bar{1})$ . The procedure is just the same, the only difference being introduced on the right-hand side of the first equation by the different indices, this side working out to  $\frac{1}{4}$  instead of  $\frac{1}{5}$ , and a 4 being substituted for a 5 in consequence in the denominator of the expression for  $\tan \theta$ . Working out the value of  $mx$  on this basis we find it to be

14° 35', an angle 2° 34' larger than the observed angle between the faces  $m$  and  $x$ , a difference far greater than any possible error even with a badly reflecting face, while the reflection from  $x$  was distinctly good. We are thus finally sure that  $x$  is  $(4\bar{2}1)$  and the angle  $mx$  12° 1'.

This completes the calculations of the interfacial angles, and we proceed lastly to calculate the elements.

The Millerian rhombohedral axes being of equal length, there is no ratio of the axes to calculate, but we have to determine the angle  $\alpha$  between the axes, that is, the angle which any pair of axes make with one another, for the three axial angles are equal, and therefore all are equally represented by  $\alpha$ .

**The Millerian Axial Angle  $\alpha$ .**—As the three polar edges of the primary rhombohedron  $\{100\}$  are chosen as the directions of the Millerian axes, the angle between the axes is equal to the plane angle between these polar rhombohedral edges. In the projection, Fig. 322, the arc joining the two poles of the primary rhombohedron (100) and (010), and passing also through the possible pole of the negative rhombohedron (110), represents one of these polar edges, the zone-axis of the zone-circle of which the arc is part being parallel to this polar edge. Similarly, arcs joining (100) to (001), and (001) to (010), represent the other two edges. The angle of intersection of any two of these three arcs will consequently be the supplement of the axial angle  $\alpha$ .

We can readily calculate the half of this supplementary angle,  $\frac{180-\alpha}{2}$ , for it is the angle at (100) in the triangle (100):(111):(110), in which the angle at (110) is a right angle. For we know two other elements in this triangle, namely, the angle at (111) which is 60°, and the side (100):(111), which is the complement 51° 47' of the basal angle  $mr$  38° 13'.

Constructing the Napierian diagram, we at once obtain :

$$\begin{aligned} \cos 51^\circ 47' &= \cot 60^\circ \cot [\text{angle at (100)}] \\ \text{or } \cot [\text{angle at (100)}] &= \cos 51^\circ 47' \tan 60^\circ. \\ \text{Angle at (100)} &= 43^\circ 1\frac{1}{2}'. \end{aligned}$$

$$\begin{aligned} \text{Thus } \frac{180-\alpha}{2} &= 43^\circ 1\frac{1}{2}' \\ 180-\alpha &= 86^\circ 3' \\ \alpha &= 93^\circ 57'. \end{aligned}$$

This value of  $\alpha$  agrees precisely, to within half a minute, with the Millerian axial angle of quartz given by von Groth.

From the same triangle we can calculate another important angle which is often given along with the elements, namely the angle of the primary rhombohedron,  $rr = (100):(010)$ , the angle over each polar edge. From the diagram we at once get the value of half this angle, (100):(110), for

$$\begin{aligned} \sin [(100):(110)] &= \sin 60^\circ \sin 51^\circ 47'. \\ (100):(110) &= 42^\circ 53' \end{aligned}$$

$$\therefore \text{the rhombohedron angle } rr = (100):(010) = 85^\circ 46'.$$

This is the currently accepted value of the rhombohedral angle of quartz.

**The Bravais-Miller Axial Ratio.**—In order to calculate the relative lengths of the vertical axis  $c$  and of any one of the three equal horizontal axes, we only require to know the inclination of any face inclined to both axes, and preferably for simplicity of one the pole of which lies in the plane of the two axes, that is, the inclination of any face inclined to both axes and perpendicular to their plane. The pole of such a face will lie in the projection on the Bravais-Miller axial diameter representing the horizontal axis in question. The indices, of course, must be known, and the case is simplest when the face is a primary one.



In the case of the crystal of quartz under investigation there is such a primary form on a Bravais-Miller axis, namely, the form  $s$ , the face  $(2\bar{1}\bar{1}1)$  of which,  $(4\bar{2}1)$  in Millerian notation, lies on the axial radius  $+A_1$  (see Fig. 284 on page 338 for Bravais-Miller stereographic projection). The indices inform us that this face cuts the  $A_1$  axis at the unit parametral distance  $a$ , and that it meets the  $c$  axis at twice the unit length, for the intercepts are  $1\bar{2}\bar{2}2$ ; and that it is normal to the plane of these two rectangular axes. The conditions are those of the triangle in Fig. 324. Now, the angular position of the face, although not measured directly on the Bravais-Miller axial diametral zone owing to the absence of other faces in that possible zone, can be readily calculated, for the angle between the possible prism face  $(2\bar{1}\bar{1}0)$ , the Millerian  $(1\bar{1}0)$ , the pole of which is at the end of the same diameter, and the face  $s$  in question, is one of the angles in the triangle of which the third pole is  $m$   $(2\bar{1}\bar{1})$ , the Napierian diagram for which has already been constructed and used to find  $ms$  and from which we now also at once get:

$$\sin [(2\bar{1}\bar{1}0) : s] = \tan 30^\circ \cot s = \tan 30^\circ \cot 54^\circ 22\frac{1}{2}' \\ (2\bar{1}\bar{1}0) : s = 24^\circ 26\frac{1}{2}'.$$

Now this angle  $24^\circ 26\frac{1}{2}'$  is that between the normals to  $(2\bar{1}\bar{1}0)$  and  $(2\bar{1}\bar{1}1)$ , and is equal to the top acute angle in Fig. 324. From this triangle we then have:

$$\frac{OA}{OC} = \frac{a}{2c} = \tan 24^\circ 26\frac{1}{2}', \text{ and therefore } \frac{a}{c} = 2 \tan 24^\circ 26\frac{1}{2}'.$$

Hence

$$\frac{c}{a} = \frac{\cot 24^\circ 26\frac{1}{2}'}{2} = \frac{2.2002}{2} = 1.1001.$$

We can also readily find  $\frac{c}{a}$  from the angle between any face of the primary rhombohedron and the hexagonal prism face adjacent to it, say the front face  $(10\bar{1}1)$  and the prism face  $(10\bar{1}0)$ . If Fig. 325 represent the upper half of the combination of the two primary (direct and inverse) rhombohedra, the face  $+A_1, -A_3$ ,  $C$  is the one in question.  $OA_1$  and  $OA_3$  are the two horizontal Bravais-Miller axes which it meets, of unit length  $a$ , and  $OC$  is the vertical axis, of the unit length  $c$ . Thus:

$$\frac{c}{a} = \frac{OC}{OA_1} \text{ or } \frac{OC}{OA_3}.$$

If  $A_1 A_3$  be bisected at  $M$ , then:

$$\frac{OC}{OM} = \tan [\text{complement of basal angle } (10\bar{1}1) : (10\bar{1}0)] \\ = \tan 51^\circ 47'.$$

Now in the plane triangle  $OMA_1$  or  $OMA_3$  the angle at  $O$  is  $30^\circ$  and the angle at  $A_1$  or  $A_3$  is  $60^\circ$ , the angle at  $M$  being a right angle. Hence:

$$\frac{OM}{OA_3} = \frac{\sqrt{3}}{2}, \text{ or } OA_3 = \frac{2}{\sqrt{3}} OM.$$

Substituting this value for  $OA_3$  (or  $OA_1$ ) we get:

$$\frac{c}{a} = \frac{\sqrt{3} OC}{2 OM} = \frac{\sqrt{3}}{2} \tan 51^\circ 47' = 1.0999.$$

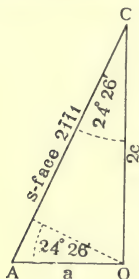


FIG. 324.

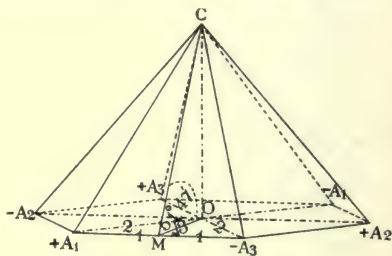


FIG. 325.

Taking the mean of the two values thus obtained by independent methods for the ratio, namely, 1.1001 and 1.0999, we may confidently state the ratio of the axis as :

$a : c = 1 : 1.1000.$

This value agrees precisely with that given by Miers for the ratio.

TABULAR PRESENTATION OF RESULTS FOR CRYSTAL OF QUARTZ, SiO<sub>2</sub>.

We may now concisely express the results of the investigation of the crystal of quartz in the following table.

**Crystal-system :** Trigonal. **Class :** 18, trapezohedral.

**Millerian rhombohedral axial angle :**  $\alpha = 93^{\circ} 57'$ . Angle over polar edges of primary rhombohedron,  $85^{\circ} 46'$ .

**Bravais-Miller ratio of axes :**  $a : c = 1 : 1.1000.$

**Forms observed :**  $m = \{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$  ;  $r = \{100\} = \{10\bar{1}1\}$  ;  $r' = \{\bar{1}22\} = \{\bar{1}011\}$  ;  $s = \{4\bar{2}1\} = \{2\bar{1}\bar{1}1\}$  ;  $x = \{4\bar{2}\bar{1}\} = \{6\bar{1}\bar{5}1\}.$

**Table of angles :** the basal angle used as the foundation of the calculations is marked with an asterisk in the following table. Angles in the same zone are linked together by a bracket.

Angle.	No. of Measurements.	Limits.	Mean observed.	Calculated.	Difference.
$mm = (2\bar{1}\bar{1}) : (11\bar{2}) = (10\bar{1}0) : (01\bar{1}0)$	6	59° 53' - 60° 8'	60° 0'	60° 0'	0'
$\left\{ \begin{array}{l} mr = (2\bar{1}\bar{1}) : (100) = (10\bar{1}0) : (10\bar{1}1) \\ mr' = (211) : (\bar{1}22) = (\bar{1}010) : (\bar{1}011) \\ rr' = (100) : (\bar{1}22) = (10\bar{1}1) : (\bar{1}011) \end{array} \right\}$	6 3	38 10 - 38 16 103 28 - 103 39	38 13 103 33	* 103 34	.. 1
$\left\{ \begin{array}{l} mx = (2\bar{1}\bar{1}) : (4\bar{2}\bar{1}) = (10\bar{1}0) : (6\bar{1}\bar{5}1) \\ xs = (4\bar{2}\bar{1}) : (4\bar{2}1) = (6\bar{1}\bar{5}1) : (2\bar{1}\bar{1}1) \\ ms = (2\bar{1}\bar{1}) : (4\bar{2}1) = (10\bar{1}0) : (2\bar{1}\bar{1}1) \end{array} \right\}$	1 1 4	.. .. 37 50 - 37 59	12 1 25 54 37 55	12 1 25 57 37 58	0 3 3
$\left\{ \begin{array}{l} sr' = (4\bar{2}1) : (2\bar{1}2) = (2\bar{1}\bar{1}1) : (\bar{1}\bar{1}01) \\ sr = (214) : (001) = (\bar{1}\bar{1}21) : (0\bar{1}11) \\ r'r = (2\bar{1}2) : (001) = (\bar{1}\bar{1}01) : (0\bar{1}11) \end{array} \right\}$	4 4 4	28 48 - 29 5 46 10 - 46 35	28 58 46 18	28 54 46 16	4 2
$\left\{ \begin{array}{l} mr' = (2\bar{1}\bar{1}) : (2\bar{1}2) = (10\bar{1}0) : (\bar{1}\bar{1}01) \\ mr = (211) : (001) = (\bar{1}010) : (0\bar{1}11) \end{array} \right\}$	8	66 40 - 67 1	66 50	66 52	2

(2) *Example of Class 21. Calcite, CaCO<sub>3</sub>.*

The crystal of calcite selected for measurement as the second example of a substance crystallising in the trigonal system was an elongated hexagonal prism, about two centimetres long and half a centimetre thick, rough at one end, where it had been attached to the rock from which it had grown, but exhibiting at the free end faces of the primary (direct or positive) rhombohedron, two other rhombohedra, and two scalenohedra. As the forms of calcite are so well known, it may as well be at once stated what were the actual forms present, and in Fig. 326 a reproduction is given of the drawing made of the crystal to scale in the usual conventional parallel-lined manner, after the completion of the measurements and calculations, in elaboration of the freehand drawing preliminarily made. The mode of construction will be given in Chapter XXV. for this particular crystal of calcite.





Circle Readings.	Angles.
$\left\{ \begin{array}{l} m \ 303^{\circ} \ 10' A \\ m \ 243 \ 9 \ A \\ m \ 183 \ 8 \\ m \ 123 \ 11 \\ m \ 63 \ 14 \\ m \ 3 \ 9 \ A \\ m \ 303 \ 10 \ A \end{array} \right.$	$\left\{ \begin{array}{l} mm \ 60^{\circ} \ 1' A \\ mm \ 60 \ 1 \\ mm \ 59 \ 57 \\ mm \ 59 \ 57 \\ mm \ 60 \ 5 \\ mm \ 59 \ 59 \ A \end{array} \right.$

It is useless to take the mean of these six values of the prism angle, for in any case, as they together make up a complete circle, such mean would be  $60^{\circ} \ 0'$ . But this is obviously the zone of a hexagonal prism, for the two adjacent  $A$ -values are each within  $1'$  of  $60^{\circ} \ 0'$ . Hence, the primitive circle of the stereographic projection may at once be drawn in, showing a pole of this form at every  $60^{\circ}$ , arranged at the end of a Millerian and not a Bravais-Millerian axis in each case, as the position of the cleavage rhombohedron clearly indicates that the prism is the first order one  $\{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$  and not the second order prism  $\{10\bar{1}\} = \{11\bar{2}0\}$ .

The three equal zones, the projections of which are the three diameters obtained by joining parallel pairs of prism poles, were next measured. Each contains the two parallel prism faces  $m$ , and between them a face of the primary positive rhombohedron  $r = \{100\}$  and a face of the obtuse negative rhombohedron  $e = \{110\}$ , and one of the zones also comprises the single developed face of the acute positive rhombohedron  $n = \{3\bar{1}\bar{1}\}$ . The measurements were as follows :

Circle Readings.	Angles.	Circle Readings.	Angles.	Circle Readings.	Angles.
$\left\{ \begin{array}{l} m \ 352^{\circ} \ 15' A \\ n \ 338 \ 2 \ A \\ r \ 306 \ 52 \ A \\ e \ 236 \ 2 \ A \end{array} \right.$	$\left\{ \begin{array}{l} mn \ 14^{\circ} \ 13' A \\ nr \ 31 \ 10 \ A \\ mr \ 45 \ 23 \ A \\ re \ 70 \ 50 \ A \end{array} \right.$	$\left\{ \begin{array}{l} m \ 228^{\circ} \ 27' A \\ e \ 164 \ 47 \ A \\ r \ 93 \ 50 \ A \\ m \ 48 \ 26 \ A \end{array} \right.$	$\left\{ \begin{array}{l} me \ 63^{\circ} \ 40' A \\ er \ 70 \ 57 \ A \\ rm \ 45 \ 24 \ A \end{array} \right.$	$\left\{ \begin{array}{l} m \ 236^{\circ} \ 20' \\ e \ 172 \ 32 \ A \\ r \ 101 \ 38 \\ m \ 56 \ 16 \end{array} \right.$	$\left\{ \begin{array}{l} me \ 63^{\circ} \ 48' \\ er \ 70 \ 54 \\ rm \ 45 \ 22 \end{array} \right.$

We may now collect the three values of  $mr$ , of  $re$ , and of  $em$ , and take the mean in each case ; for this is quite legitimate as the three angles of each such zone are widely different, while the three zones are undoubtedly exactly alike. For instance, the three values of  $mr$  only differ by  $2'$ . We then find these mean values to be  $45^{\circ} \ 23'$ ,  $70^{\circ} \ 54'$ , and  $63^{\circ} \ 44'$  respectively.

We had next another series of equal zones to measure, namely those represented by the circular arcs drawn symmetrically to each diameter, beginning at one end of the diameter and finishing at the other end, thus connecting a pair of parallel prism faces again, but including in this zone only a primary rhombohedron face  $r$ , and, when developed, a common scalenohedron face  $v$ . As two of the scalenohedron faces were developed, the two such zones containing them were measured, and gave the following results :

Circle Readings.	Angles.	Circle Readings.	Angles.
$\left\{ \begin{array}{l} m \ 18^{\circ} \ 40' A \\ r \ 309 \ 17 \ A \\ v \ 226 \ 52 \ A \\ m \ 198 \ 40 \ A \end{array} \right.$	$\left\{ \begin{array}{l} mr \ 69^{\circ} \ 23' A \\ rv \ 82 \ 25 \ A \\ vm \ 28 \ 12 \ A \end{array} \right.$	$\left\{ \begin{array}{l} m \ 230^{\circ} \ 17' A \\ v \ 202 \ 21 \\ r \ 119 \ 49 \\ m \ 50 \ 17 \end{array} \right.$	$\left\{ \begin{array}{l} mv \ 27^{\circ} \ 56' \\ vr \ 82 \ 32 \\ rm \ 69 \ 32 \end{array} \right.$

The mean values of  $mv$ ,  $vr$ , and  $rm$  in these zones are thus  $28^{\circ} 4'$ ,  $82^{\circ} 29'$ , and  $69^{\circ} 28'$  respectively. As regards the construction of the arcs representing these zones in the projection, it is only necessary both for this purpose and that of constructing the only remaining arcs on the projection, those for the next series of zones to be considered, to find the positions of the poles  $r$  and  $e$  on any one of the Millerian diameters. This is done, as indicated in Chapter VI., by setting off from the end of the diameter, the pole  $m$ , an arc along the primitive circle equal to the measured angle  $mr$  or  $me$ , and joining this point thus found on the primitive circle to the pole of the zone of which the diameter is the projection, that is, to the end lying on the primitive circle of a diameter perpendicular to the one in question, dotted in Fig. 327. The line of junction passes through the pole of the face  $r$  or  $e$  as the case may be. It is necessary to draw all three dotted diameters, perpendicular to the three Millerian ones joining prism poles, for these diameters are the Bravais-Miller axes, and their ends are the ends also of arcs representing zones passing through the facial poles  $v$ ,  $r$ ,  $t$ ,  $e$ , a second  $t$ , and a second  $r$ . Having found the poles  $r$  and  $e$  on one of the Millerian diameters by the usual method just indicated, the poles of these forms on the other two Millerian diameters can be pricked off at similar positions with the compasses, the radius can be found of an arc to pass through  $m$  and the facial pole  $r$  lying to right or left of the diameter on which  $m$  is situated, and the arc drawn. Six such equal and similar arcs can be constructed as shown in Fig. 327, and in the case of the two comprising also the scalenohedron faces  $v$  the pole of one such  $v$ -face will also lie on the arc, in a position to be presently indicated. Similarly three further arcs may also be drawn, terminating at the ends of a Bravais-Miller diameter in each case, to pass through the facial pole  $e$  which lies on the Millerian diameter at right angles to it; such an arc will also, as above mentioned, pass through two  $r$  facial poles, and two poles of the scalenohedron  $t$ , as well as one of the common scalenohedron poles  $v$  in the case of two of the three arcs so drawn. The fact that each pole of the common scalenohedron  $v$  lies both on one of the six former arcs ending at an  $m$  facial pole, and on one of the three latter arcs terminating at the ends of a Bravais-Millerian diameter, determines at once the position of the  $v$  pole, namely, at the intersection of the two zonal arcs. The position of the acute positive rhombohedron  $n$  must be found in the same manner as the poles  $r$  and  $e$  were found, namely, by cutting off an angle along the primitive circle equal to the measured angle  $mn$ , and joining this point to the pole of the diametral zone, that is, to the end of the perpendicular (dotted) diameter on the other side to that on which the arc was marked off. The poles of all the forms present have now been located on the projection except those of the scalenohedron  $t$ . We have next to proceed to the measurement of the three zones last alluded to, terminating at the ends of Bravais-Millerian diameters, and in doing so we shall locate the position of the  $t$  poles, and enable their places also to be marked on the projection. The actual measurements gave the following results:

Circle Readings.	Angles.	Circle Readings.	Angles.	Circle Readings.	Angles.
$\left\{ \begin{array}{l} v \ 237^{\circ} \ 5' \\ r \ 208 \ 1 \ A \\ t \ 191 \ 34 \\ e \ 170 \ 36 \\ r \ 133 \ 7 \ A \end{array} \right.$	$\left\{ \begin{array}{l} vr \ 29^{\circ} \ 4' \\ rt \ 16 \ 27 \\ te \ 20 \ 58 \\ re \ 37 \ 25 \\ er \ 37 \ 29 \\ rr \ 74 \ 54 \end{array} \right.$	$\left\{ \begin{array}{l} v \ 271^{\circ} \ 34' \\ r \ 242 \ 30 \ A \\ t \ 226 \ 3 \\ e \ 205 \ 8 \\ r \ 167 \ 38 \end{array} \right.$	$\left\{ \begin{array}{l} vr \ 29^{\circ} \ 4' \ A \\ rt \ 16 \ 27 \\ te \ 20 \ 55 \\ re \ 37 \ 22 \\ er \ 37 \ 30 \\ rr \ 74 \ 52 \end{array} \right.$	$\left\{ \begin{array}{l} r \ 264^{\circ} \ 10' \\ e \ 226 \ 42 \\ r \ 189 \ 14 \end{array} \right.$	$\left\{ \begin{array}{l} re \ 37^{\circ} \ 28' \\ er \ 37 \ 28 \\ rr \ 74 \ 56 \end{array} \right.$

Collecting similar angles and taking means we find that the mean value of  $vr$  is  $29^{\circ} 4'$ , of  $rt$   $16^{\circ} 27'$ , of  $te$   $20^{\circ} 57'$ , of  $re$   $37^{\circ} 27'$ , and of  $rr$   $74^{\circ} 54'$ .

We can now find the positions of the poles of  $t$  on the projection. Taking the  $t$  pole to the right of the vertical diameter ( $2\bar{1}\bar{1}$ ) : ( $\bar{2}11$ ) for instance, on the arc ending on the horizontal dotted diameter, we first find the pole of the arc itself, namely, that which bears the poles ( $0\bar{1}1$ ),  $r=(001)$ ,  $e=(011)$ ,  $t=(031)$ ,  $r=(010)$ ,  $v=(02\bar{1})$ , ( $0\bar{1}1$ ). To do so we join ( $0\bar{1}1$ ) to  $e=(011)$  and produce the straight line of junction to meet the primitive circle; from this point on the primitive circle downwards we mark off a quadrant arc, and join this point thus marked off to the starting-point ( $0\bar{1}1$ ). Where this junction line cuts the diameter ( $2\bar{1}\bar{1}$ ) : ( $\bar{2}11$ ) is the required pole  $P$  of the zonal arc. We have now only to mark off the angle  $et=20^{\circ} 57'$  (or adequately closely  $21^{\circ}$ ) from  $m=(\bar{2}11)$  along the primitive circle to the right, and join this point to  $P$ , the pole of the zone just found. Where this line cuts the zonal arc is the position of the pole  $t=(031)$ .

One further measurement was made, namely, of the angle between the two common scalenohedron faces,  $vv$ , which was found to be  $35^{\circ} 39'$ . There are no other faces in the same zone, those of the second order hexagonal prism, which would be in the same zone if present, not being developed on this crystal of calcite.

This completes the angular measurements necessary for the determination of the crystal elements and the verification of the symmetry.

The indices of the forms  $n$ ,  $v$ , and  $t$ , which were preliminarily assigned to these forms as the result of the knowledge of their positions gained during the measurements, and which corresponded to the well-known positions of the chief forms of calcite, will be found to be fully confirmed during the course of the calculations, to which we may now proceed. The indices of  $v$  are, moreover, at once confirmed by cross-multiplication of the indices of the two zones on which each scalenohedron face lies.

**Calculation of Angles and Elements.—Basal Angle,  $mr=(2\bar{1}\bar{1}) : (100) = 45^{\circ} 23'$ .**

It follows immediately, from the value of the basal angle  $mr$ , that its complement  $(100) : (111)$  is  $44^{\circ} 37'$ .

**To find  $re=(100) : (110)$  and  $(111) : (110)$ .**

These angles can both be calculated from the triangle  $r=(100)$ ,  $(111)$ ,  $e=(110)$ , in which the angle at  $e$  is a right angle, the angle at  $(111)$  is  $60^{\circ}$ , and the side  $(111) : (100)$  has just been shown to be  $44^{\circ} 37'$ .

Constructing a Napierian diagram, we at once derive from it according to Napier's rules:

$$\begin{aligned} \cos 60^{\circ} &= \cot 44^{\circ} 37' \tan (111 : e) \\ \tan (111 : e) &= \cos 60^{\circ} \tan 44^{\circ} 37' \quad | \quad \sin re = \sin 60^{\circ} \sin 44^{\circ} 37' \\ 111 : e &= 26^{\circ} 16'. \qquad \qquad \qquad re = 37^{\circ} 28'. \end{aligned}$$

From which :  $rr=(100) : (010) = 2 re = 74^{\circ} 56'$ .

The measured value of  $rr$  was  $74^{\circ} 54'$ , which agrees satisfactorily with this calculated value. This angle over the polar edges of the primary rhombohedron  $\{100\}$  is the well-known rhombohedral angle of calcite, and the angle of the cleavage rhombohedron of the mineral.

**To find  $rm=(100) : (11\bar{2})$ .**

This angle can be found from the triangle  $m=(2\bar{1}\bar{1})$ ,  $r=(100)$ ,  $m=(11\bar{2})$ , in which there is a right angle at  $m=(2\bar{1}\bar{1})$ , the side  $mm$  is  $60^{\circ}$ , and the side  $m=(2\bar{1}\bar{1}) : r=(100)$  is the basal angle  $45^{\circ} 23'$ . From the Napierian diagram we at once get by the rules:

$$\cos rm = \cos 45^{\circ} 23' \cos 60^{\circ}. \quad rm = 69^{\circ} 28'.$$

This agrees well with the mean of the two measured values,  $69^{\circ} 28'$ .



We come next to the problem of finding the position of the scalenohedron face  $v=(20\bar{1})$ , in the zone  $(10\bar{1})$ ,  $v=(20\bar{1})$ ,  $r=(100)$ ,  $e=(101)$ , that is :

To find the angle  $rv=(100):(20\bar{1})$ .

This is achieved by means of the anharmonic ratio of four poles in a zone, and the problem is the simpler by reason of the fact that the whole angle from  $(10\bar{1})$  to  $e=(101)$  is  $90^\circ$ . The conditions are clearly shown in Fig. 328, from which we at once deduce, in accordance with the method explained in Chapter VI. :

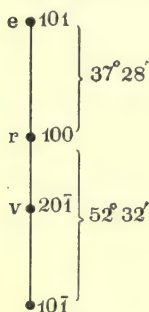


FIG. 328.

$$\frac{10\bar{1}}{20\bar{1}} \cdot \frac{101}{101} = \frac{\sin(10\bar{1}):v}{\sin 52^\circ 32'} \cdot \frac{\sin 37^\circ 28'}{\sin ev}$$

$$\frac{1}{1} \cdot \frac{1}{3} = \frac{1}{3} = \frac{\sin(10\bar{1}):v}{\sin ev} \cdot \frac{\sin 37^\circ 28'}{\sin 52^\circ 32'}$$

$$\frac{1}{3} = \frac{\sin(10\bar{1}):v}{\cos(10\bar{1}):v} \cdot \frac{\sin 37^\circ 28'}{\cos 37^\circ 28'}$$

$$= \tan(10\bar{1}):v \cdot \tan 37^\circ 28'$$

$$\tan(10\bar{1}):v = \frac{1}{3} \cot 37^\circ 28'. \quad (10\bar{1}):v = 23^\circ 30'.$$

$$\text{Then } vr = [(10\bar{1}):r] - [(10\bar{1}):v] = 52^\circ 32' - 23^\circ 30' = 29^\circ 2'.$$

The mean observed value of this angle was  $29^\circ 4'$ .

To find  $mv=(2\bar{1}1):(20\bar{1})$ .

The magnitude of this angle  $mv$  may be readily calculated from the triangle  $m=(2\bar{1}1)$ ,  $r=(100)$ ,  $v=(20\bar{1})$ , in which we know the two sides  $mr=45^\circ 23'$  and  $vr=29^\circ 2'$  and the angle between them; for this latter is the same as the angle at  $r$  in the first triangle dealt with. Working out first this angle  $r$  from the Napierian diagram we have :

$$\cos r = \sin 60^\circ \cos 26^\circ 16' (111:e). \quad r=39^\circ 3'.$$

Having now our three known elements in the oblique-angled triangle  $mrv$ , we apply formula (b) of the few ordinary essential formulæ of spherical trigonometry given in Chapter VII., page 109, from which we get :

$$\tan \theta = \tan 29^\circ 2' \cos 39^\circ 3'; \quad \cos mv = \frac{\cos 29^\circ 2' \cos (45^\circ 23' - \theta)}{\cos \theta}.$$

$$\theta = 23^\circ 19'.$$

$$mv = 28^\circ 4'.$$

This value  $28^\circ 4'$  is identical with the mean of the measured values of  $mv$ .

To find  $vv=(20\bar{1}):(2\bar{1}0)$ .

The half of this angle,  $vN$ , can easily be found, as it forms one of the sides adjacent to the right angle in the triangle of which the other two sides are  $r=(100):v=(20\bar{1})$ , and the part  $Nr$  of  $m=(2\bar{1}1):r=(100)$  on the upper or  $r$  side of its intersection by the arc  $vv$  in question. The angle at  $r$  is the same as occurred in the last triangle, namely,  $39^\circ 3'$ , the side  $rv$  is  $29^\circ 2'$ , and the angle at the intersection  $N$  of  $mr$  and  $vv$  is a right angle. Hence, from the Napierian diagram we have :

$$\sin \frac{1}{2} vv = \sin 29^\circ 2' \sin 39^\circ 3'. \quad \frac{1}{2} vv = 17^\circ 48', \quad vv = 35^\circ 36'.$$

The measurement of  $vv$  gave the value  $35^\circ 39'$ .

It now only remains, as regards the angular magnitudes, to determine the positions of the faces of the rhombohedron  $n=\{3\bar{1}1\}$  and of the scalenohedron  $t=\{310\}$ .

To find the position of  $n=\{3\bar{1}1\}$  in the zone  $[mnr]$ .

The four poles consisting of the three just mentioned and  $(111)$  are situated on and together make up a quadrant, so we have the simpler case of the anharmonic ratio of four poles in a  $90^\circ$  zone. Setting forth the conditions along the usual linear diagram, similarly to Fig. 328, we obtain the following :

$$\begin{array}{c} \frac{\sin mn}{\sin 45^\circ 23'} \cdot \frac{\sin 44^\circ 37'}{\sin (111:n)} = \frac{2\bar{1}\bar{1}}{3\bar{1}\bar{1}} \cdot \frac{111}{100} \\ \frac{\sin mn}{\cos mn} \cdot \frac{\sin 44^\circ 37'}{\cos 44^\circ 37'} = \frac{1}{1} \cdot \frac{\bar{1}}{4} = \frac{1}{4} \\ \tan mn = \frac{1}{4} \cot 44^\circ 37'. \quad mn = 14^\circ 13'. \end{array}$$

Then :  $nr = mr - mn = 45^\circ 23' - 14^\circ 13' = 31^\circ 10'$ .

Each of these values is identical with the single measured value.

Similarly, to find the position of  $t = \{301\}$  in the  $90^\circ$ -zone comprising the four poles ( $10\bar{1}$ ),  $r = \{100\}$ ,  $t = \{301\}$ ,  $e = \{101\}$ , we draw the linear diagram, and from the conditions therein set out we at once derive the ratio :

$$\begin{array}{c} \frac{\sin 52^\circ 32'}{\sin (10\bar{1}) : t} \cdot \frac{\sin et}{\sin 37^\circ 28'} = \frac{10\bar{1}}{100} \cdot \frac{101}{301} \\ \frac{\sin et}{\cos et} \cdot \frac{\cos 37^\circ 28'}{\sin 37^\circ 28'} = \frac{1}{4} \cdot \frac{2}{1} = \frac{1}{2} \\ \tan et = \frac{1}{2} \tan 37^\circ 28'. \quad et = 20^\circ 58'. \end{array}$$

Then  $tr = 37^\circ 28' - 20^\circ 58' = 16^\circ 30'$ .

The measured values of these two angles, each the mean of two measurements, were  $20^\circ 57'$  and  $16^\circ 27'$  respectively.

The agreement of both these values for the position of the scalenohedron  $t = \{310\}$ , as also of both those for the position of the rhombohedron  $n = \{3\bar{1}\bar{1}\}$ , with the measured values is so satisfactory that absolute proof is afforded that the indices provisionally assigned to those two forms, namely  $\{310\}$  and  $\{3\bar{1}\bar{1}\}$ , are correct. It will be obvious that the method of the anharmonic ratio can be used, as shown in Chapter VI., either for the calculation of the angles, assuming the indices, as has just been done, or for the determination of the indices, assuming the angles. As a matter of fact, as soon as the angles had been measured, the method was used to arrive provisionally at the proper indices, assuming the measured values to be correct. For instance, as regards the indices of the pole  $n$ , the left-hand side of the equation, assuming the measured angle,  $mn = 14^\circ 13'$ , to be correct, became :  $\tan 14^\circ 13' \cdot \tan 44^\circ 37'$ , the actual value of which is  $\frac{1}{4}$ .

For  $\tan 14^\circ 13' \tan 44^\circ 37' = 0.24998 = \frac{1}{4}$ , or  $\frac{\tan 44^\circ 37'}{\tan 75^\circ 47'} = \frac{0.9867}{3.9471} = \frac{1}{4}$ .

The right hand side of the equation, if the indices of  $n$  are  $(pqg)$ , is :

$$\begin{array}{c} \frac{2\bar{1}\bar{1}}{pqq} \cdot \frac{100}{111} = \frac{2q+p}{1} \cdot \frac{\bar{1}}{q-p} = \frac{-2q-p}{q-p}; \\ \frac{100}{pqq} \end{array}$$

Hence, equating the two sides to each other :

$$\frac{1}{4} = \frac{-2q-p}{q-p}, \text{ or } q-p = -8q-4p,$$

that is :

$$9q = -3p, \text{ or } \frac{p}{q} = \frac{9}{3} = \frac{3}{1}.$$

From which we gather that  $p=3$ , and  $q=-1$ , so that the indices of  $n$  are  $(3\bar{1}\bar{1})$

In a similar manner, the indices of the particular face of  $t$  in the next zone dealt with, [ $etr$ ], were provisionally found to be (301), assuming the angle  $et$  to have the measured value  $20^\circ 57'$ . The final confirmation of the measured angles, by the calculations of those angles from the basal angle, now completes the proof of the correctness, both of the indices and of the positions of the forms  $n$  and  $t$ .

**The Millerian Axial Angle  $\alpha$ .**—As shown in the case of quartz, the angle of intersection of a pair of zones [ $rer$ ] is the supplement of the axial angle. For each arc  $rer$  represents the angle over the polar edge between two primary rhombohedron faces, the well-known rhombohedral angle, and the angle between such a pair of edges is by the very mode of choice of the Millerian axes the angle between the axes, for the edges are the chosen directions of the axes. Now half the angle of intersection of these arcs, namely, the angle at  $r$  in the triangle  $r=(100)$ ,  $o=(111)$ ,<sup>1</sup>  $e=(110)$ , has already been calculated and shown to be  $39^\circ 3'$ . Hence, the angle of intersection itself is  $78^\circ 6'$ . This is obviously the acute angle between the axes, and the one required, representing the obtuse angle between the two polar edges bounding the rhombohedron face, is consequently the supplement of this, or:

$$\alpha = 180^\circ - 78^\circ 6' = 101^\circ 54'.$$

Von Groth gives  $101^\circ 55'$  for this angle, so that our measurements have evidently been satisfactorily accurate.

**The Bravais-Miller Axial Ratio.**—There is no face developed on the crystal, the pole of which would lie on a Bravais-Miller axis (dotted in Fig. 327). But we can find the ratio  $\frac{a}{c}$  by the same method as was employed (second method) in the case of quartz, from the angle  $r=(100):o=(111)$  in the same triangle as has just been used for obtaining the Millerian axial angle, namely,  $roe$ . This angle is the complement of the basal angle, namely,  $44^\circ 37'$ , and from the discussion of the same case for quartz (page 370) it will be clear that the relationship between this angle and the Bravais-Miller axial ratio is:

$$\frac{c}{a} = \frac{\sqrt{3}}{2} \tan 44^\circ 37'.$$

Calculating this out, we obtain  $\frac{c}{a} = 0.8545$ .

Hence:

$$a:c = 1:0.8545.$$

The value of the ratio given by Kuppfer is  $1:0.8543$ , which is a very good concordance.

#### TABULAR PRESENTATION OF RESULTS FOR CRYSTAL OF CALCITE, $\text{CaCO}_3$ .

**Crystal system:** Trigonal. **Class:** 21, scalenohedral.

**Millerian rhombohedral axial angle:**  $\alpha = 101^\circ 54'$ . Angle of primary rhombohedron  $\{100\}$  (over polar edges)  $= 74^\circ 56'$ .

**Bravais-Miller ratio of axes:**  $a:c = 1:0.8545$ .

**Forms observed:**  $m = \{2\bar{1}\bar{1}\} = \{10\bar{1}0\}$ ,  $r = \{100\} = \{10\bar{1}1\}$ ,  $e = \{110\} = \{01\bar{1}2\}$ ,  $n = \{3\bar{1}\bar{1}\} = \{40\bar{4}1\}$ ,  $v = \{20\bar{1}\} = \{21\bar{3}1\}$ ,  $t = \{310\} = \{21\bar{3}4\}$ .

<sup>1</sup> It is convenient to denote the pole of the undeveloped basal plane (111) by the letter  $o$ .



**Table of angles :** The basal angle is marked with an asterisk ; the large brackets indicate the zones.

Angle.	No. of Measurements.	Limits.	Mean observed.	Calculated.	Difference.
$mm = (2\bar{1}\bar{1}) : (11\bar{2}) = (10\bar{1}0) : (01\bar{1}0)$	6	59° 57'–60° 5'	60° 0'	60° 0'	0'
$\left\{ \begin{array}{l} mn = (2\bar{1}\bar{1}) : (3\bar{1}\bar{1}) = (10\bar{1}0) : (40\bar{1}1) \\ nr = (3\bar{1}\bar{1}) : (100) = (40\bar{1}1) : (10\bar{1}1) \\ mr = (2\bar{1}\bar{1}) : (100) = (10\bar{1}0) : (10\bar{1}1) \\ ro = (100) : (111) = (10\bar{1}1) : (0001) \\ oe = (111) : (011) = (0001) : (10\bar{1}2) \\ re = (100) : (011) = (10\bar{1}1) : (10\bar{1}2) \\ em = (011) : (211) = (10\bar{1}2) : (10\bar{1}0) \end{array} \right.$	 1 1 3 .. .. 3 3	 .. .. 45 22–45 24 .. .. 70 50–70 57 63 40–63 48	 14 13 31 10 45 23 .. .. 70 54 63 44	 14 13 31 10 * 44 37 26 16 70 53 63 44	 0 0 .. .. .. 1 0
$\left\{ \begin{array}{l} mv = (2\bar{1}\bar{1}) : (20\bar{1}) = (10\bar{1}0) : (21\bar{3}1) \\ vr = (20\bar{1}) : (010) = (21\bar{3}1) : (1101) \\ rm = (010) : (211) = (1101) : (10\bar{1}0) \end{array} \right.$	 2 2 2	 27 56–28 12 82 25–82 32 69 23–69 32	 28 4 82 29 69 28	 28 4 82 30 69 26	 0 1 2
$\left\{ \begin{array}{l} vr = (20\bar{1}) : (100) = (21\bar{3}1) : (10\bar{1}1) \\ rt = (100) : (301) = (10\bar{1}1) : (3\bar{1}\bar{2}4) \\ te = (301) : (101) = (3\bar{1}\bar{2}4) : (1102) \\ re = (100) : (101) = (10\bar{1}1) : (1102) \\ rr = (100) : (001) = (10\bar{1}1) : (01\bar{1}1) \end{array} \right.$	 2 2 2 6 3	 29 4–29 4 16 27–16 27 20 55–20 58 37 22–37 30 74 52–74 56	 29 4 16 27 20 57 37 27 74 54	 29 2 16 30 20 58 37 28 74 56	 2 3 1 1 2
$vv = (20\bar{1}) : (210) = (21\bar{3}1) : (3\bar{1}\bar{2}1)$	1	..	35 39	35 36	3

In concluding these practical examples of the method of carrying out the morphological investigation of crystals, it may be remarked that the only difference between the method here shown and the actual investigation of a newly discovered, and therefore hitherto unmeasured, crystallised substance, is that instead of one crystal being so investigated at least ten of the very best procurable crystals should be measured, selected from at least four different crops if it be an artificially prepared substance, in order that as many excellent “A” values of each of the angles may be obtained as possible from which to extract the mean value, and so that we may be reasonably sure that all the forms developed by the substance, which may not all be present on a single crystal, or on any of the crystals of a particular crop, have been observed.

## CHAPTER XXIV

### CLOSENESS OF ANGLES OF ISOMORPHOUS SALTS, AND CONSEQUENT NECESSITY FOR ACCURACY—TREATMENT OF SPECIAL DIFFICULTIES IN CRYSTAL MEASUREMENT, AND PITFALLS TO BE AVOIDED

THE object of this chapter is to emphasise how essential it is that the highest possible accuracy should be aimed at and attained, in the cases of all goniometrical measurements the results of which are intended to be published as contributions to the original literature of the subject. The publication in the past of angular values derived by measurement of the crystals of substances of a low order of purity, of crystals of imperfect and more or less distorted form, and by the use of goniometers of doubtful accuracy, has introduced grave errors and indeed complete misconceptions into crystallographic literature which it will require years of patient accurate work to correct. In former times, during the infancy of chemistry and crystallography, and before the perfection of goniometrical methods, this was unavoidable; but to-day there is absolutely no excuse for the publication of immature and imperfect work, and the author desires to plead most earnestly for greater accuracy, and particularly for the avoidance of all premature publication.

**The Importance of Accurate Goniometry.**—A most instructive example of what is meant is afforded by the group of rhombic salts of which the typical example, potassium sulphate,  $K_2SO_4$ , so often referred to in this book and which is illustrated in the first three figures in Chapter I., is the first member, namely, the sulphates of the alkali metals potassium, rubidium, and caesium. Previous to the author's reinvestigation of these salts, the values currently accepted for the ratios of the crystallographic axes were the early ones of Mitscherlich for potassium sulphate dating from the year 1830, Bunsen's values for rubidium sulphate published in 1861, and those given by Topsøe from measurements made by von Lang in 1867 for caesium sulphate. These values are as follows:

$$\begin{array}{l} \text{For } K_2SO_4 \quad a : b : c = 0.5727 : 1 : 0.7464 \\ \text{,, } Rb_2SO_4 \quad a : b : c = 0.5723 : 1 : 0.7522 \\ \text{,, } Cs_2SO_4 \quad a : b : c = 0.5805 : 1 : 0.7400 \end{array}$$

Now these numbers show no progression according to the atomic

weight or atomic number of the alkali metal, and indeed no relationship whatsoever, beyond the fact of mere similarity in the kind of values. No definite law was obviously indicated by them. But the result of the author's investigations,<sup>1</sup> taking all the precautions which have been recommended in this book and employing all the resources now available for refined work, has been to show that this promiscuous order of these ratios is incorrect and totally misleading, and that their true order is as under :

$$\begin{aligned}\text{For } K_2SO_4 \quad a : b : c &= 0.5727 : 1 : 0.7418 \\ \text{,, } Rb_2SO_4 \quad a : b : c &= 0.5723 : 1 : 0.7485 \\ \text{,, } Cs_2SO_4 \quad a : b : c &= 0.5712 : 1 : 0.7531\end{aligned}$$

Remembering that the atomic weight of potassium is 38.85, that of rubidium 84.9, and that of caesium 131.9 (when hydrogen=1), and that the atomic weight of rubidium is thus about the mean (85.4) of the atomic weights of potassium and caesium, it will be obvious that the true order of the axial ratios is the same as the order of the atomic weights. This is particularly noticeable in the case of the ratio of  $c : b$ , where the differences between the values are far removed from the neighbourhood of the possible experimental error of these refined measurements. The order is also the same as that of the atomic numbers (the sequence numbers of the chemical elements when arranged in order of their atomic weights, in the periodic table). For the atomic number of potassium is 19, that of rubidium 37 (difference 18), and that of caesium 55 (difference again 18); the atomic number of rubidium is thus likewise the mean of the atomic numbers of potassium and caesium.

The fact which it is desired to emphasise, the absolute necessity for accuracy, is even more strikingly brought out by the interfacial angles themselves. The old accepted values were of such a promiscuous character as to be worse than useless, just as in the case of the ratios, for the only conclusions possible to be based upon them were that no law governed their relationships. The important law of progression according to atomic weight or atomic number, now fully established, crystallographically as well as chemically and physically, was never even suspected to apply in the case of the crystallographic constants, being entirely hidden and prevented from coming to light by erroneous measurements, or measurements with impure material. But when the true angular values were established as the outcome of most careful and prolonged work, a very different state of matters was revealed; for the magnitudes of the whole of the angles of rubidium sulphate, without a single exception, were found to lie between those of the analogous angles upon the potassium and caesium salts respectively. A progressive change is thus observed to be brought about in the angular magnitudes of the crystals of the sulphates of potassium, rubidium, and caesium, corresponding to the progressive change in the atomic weight or atomic number of the contained metal, when potassium is replaced by rubidium and the latter by caesium.

<sup>1</sup> See *Crystalline Structure and Chemical Constitution* (Macmillan, 1910) for a connected account of these researches.



This important fact will be clearly apparent from the table of angles of the crystals of the three salts, which is given below, and which

*Comparative Table of Interfacial Angular Magnitudes of Rhombic Alkali Sulphates and Selenates.*

Angle.	K <sub>2</sub> SO <sub>4</sub> .	Rb <sub>2</sub> SO <sub>4</sub> .	Cs <sub>2</sub> SO <sub>4</sub> .	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .	Tl <sub>2</sub> SO <sub>4</sub> .	K <sub>2</sub> SeO <sub>4</sub> .	Rb <sub>2</sub> SeO <sub>4</sub> .	Cs <sub>2</sub> SeO <sub>4</sub> .	Tl <sub>2</sub> SeO <sub>4</sub> .
$\{ap = (100) : (110)$	29° 48'	29° 47'	29° 44'	29° 24'	29° 3'	29° 49'	29° 43'	29° 41'	29° 2'
$\{pp' = (110) : (130)$	30 0	30 0	30 0	30 0	29 59	30 0	30 0	30 0	29 59
$\{p'b = (130) : (010)$	30 12	30 13	30 16	30 36	30 58	30 11	30 17	30 19	30 59
$\{cq''' = (001) : (012)$	20 21	20 31	20 38	20 6	20 7	20 6	20 16	20 22	19 55
$\{q'''q = (012) : (011)$	16 13	16 18	16 21	16 6	16 7	16 6	16 11	16 14	16 0
$\{cq' = (001) : (011)$	36 34	36 49	36 59	36 12	36 14	36 12	36 27	36 36	35 55
$\{qq' = (011) : (021)$	19 27	19 26	19 26	19 28	19 28	19 28	19 27	19 26	19 28
$\{q'q'' = (021) : (031)$	9 47	9 45	9 42	9 51	9 50	9 51	9 49	9 47	9 54
$\{q''b = (031) : (010)$	24 12	24 0	23 53	24 29	24 28	24 29	24 17	24 11	24 43
$\{q'b = (021) : (010)$	33 59	33 45	33 35	34 20	34 18	34 20	34 6	33 58	34 37
$\{ao = (100) : (111)$	43 52	43 41	43 31	43 39	43 13	44 9	43 51	43 43	43 25
$\{oq = (111) : (011)$	46 8	46 19	46 29	46 21	46 47	45 51	46 9	46 17	46 35
$\{ao' = (100) : (112)$	58 44	58 31	58 19	58 37	58 14	59 3	58 45	58 35	58 28
$\{o'o' = (112) : (112)$	62 32	62 58	63 22	62 46	63 32	61 54	62 30	62 50	63 4
$\{bo = (010) : (111)$	65 37	65 33	65 32	65 56	66 7	65 43	65 42	65 40	66 13
$\{oo = (111) : (111)$	48 46	48 54	48 56	48 8	47 46	48 34	48 36	48 40	47 34
$\{bo' = (010) : (112)$	72 42	72 37	72 33	72 56	73 0	72 51	72 47	72 43	73 8
$\{o'o' = (112) : (112)$	34 36	34 46	34 54	34 8	34 0	34 18	34 26	34 34	33 44
$\{co' = (001) : (112)$	36 44	37 0	37 13	36 42	37 2	36 21	36 41	36 52	36 44
$\{o'o = (112) : (111)$	19 27	19 26	19 25	19 27	19 26	19 28	19 27	19 26	19 27
$\{co = (001) : (111)$	56 11	56 26	56 38	56 9	56 28	55 49	56 8	56 18	56 11
$\{oo'' = (111) : (332)$	9 45	9 42	9 40	9 46	9 42	9 49	9 46	9 44	9 45
$\{o''p = (332) : (110)$	24 4	23 52	23 42	24 5	23 50	24 22	24 6	23 58	24 4
$\{op = (111) : (110)$	33 49	33 34	33 22	33 51	33 32	34 11	33 52	33 42	33 40
$\{po = (110) : (111)$	65 8	65 2	64 54	64 31	63 52	65 17	65 1	64 55	63 56
$\{oq' = (111) : (021)$	49 12	49 22	49 30	49 24	49 47	48 57	49 13	49 20	49 36
$\{q'p = (021) : (110)$	65 40	65 36	65 36	66 5	66 21	65 46	65 46	65 45	66 28
$\{po' = (110) : (112)$	72 23	72 15	72 7	71 58	71 27	72 34	72 19	72 12	71 33
$\{o'q = (112) : (011)$	34 50	35 4	35 15	34 53	35 14	34 31	34 49	34 58	34 50
$\{qp = (011) : (110)$	72 47	72 41	72 38	73 9	73 19	72 55	72 52	72 50	73 28
$\{p'o = (130) : (111)$	43 59	43 49	43 40	44 0	43 47	44 14	44 1	43 54	43 50
$\{oo' = (111) : (112)$	45 47	45 55	46 1	45 16	45 3	45 33	45 39	45 43	44 51
$\{o'q' = (112) : (021)$	46 1	46 12	46 20	46 1	46 16	45 46	45 59	46 6	46 2
$\{q'p' = (021) : (130)$	44 13	44 4	43 59	44 43	44 54	44 27	44 21	44 17	45 8
$\{p'o' = (130) : (112)$	58 48	58 35	58 25	58 50	58 33	59 6	58 51	58 42	58 48
$\{o'q = (112) : (011)$	62 12	62 36	62 53	61 43	61 54	61 36	62 1	62 16	61 24
$\{qp' = (011) : (130)$	59 0	58 49	58 42	59 27	59 33	59 18	59 8	59 2	59 48

may also serve at the same time as a specimen of how such a table of comparative angles should be drawn up, and to afford a definite idea of

the amount of the angular differences in an isomorphous series and of the limits well within which the degree of accuracy must reach. It includes also the angles of the three other isomorphous salts of these three strictly related metals of the same family group of the periodic classification of the elements, in which the sulphuric acid is replaced by selenic acid (sulphur and selenium forming isomorphous compounds); for the study of the three selenates of potassium, rubidium, and caesium has revealed precisely the same progressive relationships, and afforded an independent confirmation of the greatest value of the results with the sulphates. Moreover, the table also includes the analogous sulphates of ammonium and thallium, and thallium selenate, which are also in a broader sense isomorphous, and the results for these further salts are of particular interest as showing that the progressive changes, following the progressive atomic weights and atomic numbers, are only observed when the metals belong strictly to the same family group. A second table

*Comparative Table of Crystallographic Axial Ratios.*

Salt.	Axial Ratios.		
	<i>a</i>	<i>b</i>	<i>c</i>
K <sub>2</sub> SO <sub>4</sub> . .	0.5727	1	0.7418
Rb <sub>2</sub> SO <sub>4</sub> . .	0.5723	1	0.7485
Cs <sub>2</sub> SO <sub>4</sub> . .	0.5712	1	0.7531
Tl <sub>2</sub> SO <sub>4</sub> . .	0.5555	1	0.7328
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . .	0.5635	1	0.7319
K <sub>2</sub> SeO <sub>4</sub> . .	0.5731	1	0.7319
Rb <sub>2</sub> SeO <sub>4</sub> . .	0.5708	1	0.7386
Cs <sub>2</sub> SeO <sub>4</sub> . .	0.5700	1	0.7424
Tl <sub>2</sub> SeO <sub>4</sub> . .	0.5551	1	0.7243

is now also given in which the axial ratios of the whole series are set forth. The matter is put very concisely in the concluding paragraphs of the author's memoir on the thallium salts,<sup>1</sup> which may profitably be quoted, as they express in the clearest terms chemico-crystallographic facts which the crystal measurer should always have before him.

"The results of the investigation throw into prominent relief the main generalisation which has sprung from these researches, that in the case of an isomorphous series in the strictest sense, where the interchangeable elements belong to the same family group of the periodic classification of the elements, the whole of the properties of the crystals, morphological, optical, thermal, and physical in general, are functions of the atomic weights [or atomic numbers] of these elements. For such a series the term 'eutropic,' from *εὐτροπή*, meaning a regularly progressive change (*regelmässige Änderung*), has been suggested by Linck, and is adopted by the author.

"Where we have an element like thallium, which does not belong to

<sup>1</sup> *Proc. Roy. Soc., A*, 1907, 79, 381.

the same family group, the law does not apply, although the metal may be, as thallium is, capable of interchanging with the others without altering the crystal system, and without making angular and structural changes of much greater magnitude than those provoked by the interchange of family analogues.

"In the light of this research, the author defines an 'isomorphous series' as one the members of which bear some definite chemical analogy and crystallise according to the same system and in the same class of that system, and develop the same forms inclined at angles which only differ by a very few degrees, rarely exceeding  $3^\circ$ ; and a 'eutropic series' as one in which these small angular differences, and also the structural and physical properties of the crystals, obey the law of progression according to atomic weight [or atomic number] of the interchangeable elements which give rise to the series and which belong to the same family group.

"Thallium sulphate and selenate and ammonium sulphate (ammonium selenate is dimorphous and usually crystallises in the second, monoclinic, form) belong to the orthorhombic isomorphous series  $R_2\overset{S}{\text{Se}}\text{O}_4$ , while the sulphates and selenates of potassium, rubidium, and caesium belong not only to this same isomorphous series but also to the still more exclusive eutropic series within it."

The subject of Isomorphism will be more fully treated in a special chapter, LIV. The point which it is now desired to emphasise is that these important generalisations, lying at the root of the goniometrical relationships of definitely chemically related substances, are the direct outcome of exact measurement, and that the work of the future must partake of the same character if it is to have real and permanent value. The angular differences which have been substantiated between these isomorphous salts are remarkably small, the maximum met with, which occurs between thallium and potassium selenates in the case of one angle, being only  $1^\circ 21'$ ; in the great majority of cases they were very much smaller than this, the differences between a potassium and a caesium salt never reaching a whole degree ( $56'$  being the maximum between potassium and caesium selenates), and those between a rubidium and a potassium or caesium salt only once attaining even half a degree.

In the similar investigation which the author has carried out of the double sulphates and selenates of the monoclinic series  $R_2M(\overset{S}{\text{Se}}\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  in which R is represented by the same three alkali metals and thallium or ammonium, and which has led to the further confirmation of the law just quoted (the alkali metals exhibiting a markedly preponderating effect in determining the properties of the crystals, which consequently show precisely the same progressive angular changes following the order of the atomic weights or atomic numbers of the alkali metals), the angular changes have been found to be somewhat larger, doubtless owing to the lower degree of symmetry (monoclinic instead of rhombic); but even here the maximum difference yet met



with has only been  $2^{\circ} 28'$ , which occurs between potassium copper and caesium copper selenates in the case of one angle.

It will be clear now why a high degree of accuracy is to be aimed at, and that a few minutes of error may make a difference so weighty as to render the work of measurement not only valueless, but even productive of positively mistaken conclusions. That the crystals for use in such investigations should be as pure as the refinements of modern chemical methods render possible goes without saying, and that the great care which is inculcated in this book in regard to the growth of the crystals is really necessary will be perfectly obvious. All the precautions specified in Chapter II. should invariably be taken to avoid disturbance during the growth of the crystals, the goniometer employed should be one of the highest attainable accuracy, such as the Fuess No. 2a or the large horizontal-circle Troughton and Simms instrument, and the utmost care should be taken to exclude all angular values about which there is the slightest ambiguity, and to avoid certain pitfalls into which an inexperienced observer may very easily be precipitated, and to which attention must now be drawn.

It has been rendered abundantly plain in Chapter IV. that the image of the goniometer signal reflected by a perfect face, one which is both truly plane and brilliant, is a single, clearly defined, brightly illuminated image of the broadly terminated but centrally narrow Websky slit of the collimator. Such perfect faces are not common, and half the labour of a crystallographic investigation often consists in the many attempts which are required to grow perfect crystals before success is achieved. Trouble taken in this regard is very well spent indeed. The author has been in the habit of measuring ten such crystals of every substance which he has investigated. But if the difficulties in the way of securing ten such perfect crystals prove too great, it is far better to rely on the measurements of even one such irreproachable specimen than to take the mean of the angular values derived from both that crystal and the other nine less perfect ones. It has been amply shown in the alternate (odd-numbered) Chapters XI.-XXIII., on the goniometry of actual representative crystals of each system, that on such perfect crystals the values of analogous angles (between "A" faces), required by the symmetry to be equal, are actually so to within  $2'$  of arc, and indeed are often found to be absolutely identical (any difference being less than half a minute).

**Distorted Signal-images.**—A grossly distorted face affords naturally a correspondingly distorted image, or more frequently, an irregularly distributed bundle of distorted images. There are several pronounced types of multiple images afforded by badly distorted faces, or faces having special and peculiar properties. A very common form of image from a distorted face is a ribbon-like band of more or less overlapping images, some of which may not lie precisely in the zone, that is, may not be symmetrical to the horizontal spider-line of the telescope; the various images correspond to reflections of the signal from numerous strip-like parts of the face, the individual parts not having succeeded in quite attaining parallelism owing to disturbance of the conditions during

growth. The other specific types of faces yielding multiple images fall under two main divisions, namely, the images from striated faces, and those from closely adjacent faces of the kind known as "vicinal faces." Both these latter types of facial image merit special attention. Before proceeding to discuss them, however, it is necessary to study the effect on the signal-image of extreme narrowing of a face.

**Images from Narrow Faces.**—When a crystal face, while remaining truly plane, becomes reduced to a narrow strip,—that is, when development occurs almost entirely in one direction, possibly owing to the large development of two faces in the same zone with it and adjacent on each side, so that the face appears to be merely the blunted edge between those two largely developed faces and appears in the micro-telescope as an illuminated line, or under a higher power as an elongated strip with two long parallel sharp edges,—the phenomena of diffraction or the bending of light-waves round sharp edges begin to appear, dependent on the interference of the light waves reflected from near the two edges, the mass of light reflected from the intermediate parts of the surface becoming so reduced as no longer to drown these delicate diffraction effects. The narrow face, in fact, behaves just like the narrow slit in the well-known lantern experiment on diffraction (see Chapter XXXVII., Fig. 604). When the zone of the three faces is adjusted, the Websky signal-image from the narrow face is expanded horizontally, that is, in the direction of the measurement, rendering the latter less precise when the phenomenon becomes very pronounced. When the face is not narrower than a quarter of a millimetre little inconvenience is caused, and the image is readily placed to the vertical spider-line, the volume of light from the intermediate parts of the strip being still ample to mask all but a trace of diffraction. But when the face becomes more extremely narrow the image not only becomes inconveniently broad, but is accompanied by diffraction spectra on each side, separated from the central white image and from each other at distances which increase as the narrowness becomes more extreme, and which vary with the angle of the incident light. The weakening of the illumination of the white ordinary but now much expanded image, owing to the diminution of the area of the intermediate reflecting parts and to the production of the spectra, becomes so marked as the face approaches a mere line in width, that no trustworthy measurement can be obtained from it.

It will also be clear from the above that coloured images of the signal are always to be rejected. They are either diffraction images of the kind just alluded to, which will be the case when the face is observed to be very narrow, or they may be refracted images of the signal-slit, obtained owing to two of the faces of the zone being inclined at such an angle as to form a spectroscopic prism; they are such images as are obtained in the determination of the refractive index by means of a  $60^\circ$  prism, by the process described in Chapter XLVI. These can at once be recognised by their brilliant spectrum character, and if the lens in front of the telescope objective be placed in position so as to enable the observer to view the crystal, the face of the prism from which the light is emerging will be seen illuminated in rainbow colours.



**Striated Faces.**—When a face is finely striated, it may partake both of the character of a multitude of very narrow faces arranged in close succession, and of the nature of a diffraction grating, and such striated faces are to be most suspiciously examined, and as a general rule altogether excluded from participation in the measurements. They afford a central white image the position of which may have no crystallographic significance, varying with the nature of the striation. Striation is shown in Chapters X. and XXVIII. to be due to the rapid alternation on a single crystal of two forms of the same system, such, for instance, as the cube and the pentagonal dodecahedron in the case of pyrites (Figs. 119 and 120); or else to repetition twinning, as in the case of albite (Fig. 412), the two kinds of alternating lamellæ being excessively thin. The effect in either case is similar. So long as the strips belonging to the two alternating series of individuals are not below the limits referred to in the last section on narrow faces, the cumulative effect of each set of parallel strips belonging to either of the two forms, or the two parts of the twin, is to afford a more or less trustworthy ordinary white image of the signal, the perfection of which depends as usual upon the planeness of the strips, and each set thus affords its own image. But when the narrowness of the striæ approaches that of a line the interference phenomenon of diffraction commences, and the white central image of each set, due to the directly reflected light, is widened and its edges blurred, and it is accompanied by attendant spectra on each side; as in the case of a single very narrow face, this is owing to the interference of the light emanating from near the two edges of the fine strip, just as the light from the two edges of the slit interferes in the lantern diffraction experiment already mentioned, the colour being due to the light of the different wave-lengths in succession being the only or predominating waves which remain unextinguished by interference at the positions where they are seen. Now, as the width of the striæ still diminishes, there must come a time when the different series of diffraction phenomena will mutually interfere, each pair of adjacent striæ acting as the two edges of a slit, and the two separate series of images will become replaced by one series, the central white image of which occupies a position intermediate between the two former separate white images, corresponding to the plane tangential to the edges of the re-entrant angles formed by the two series of strip-planes; the position of this tangential plane varies with the narrowness of the strips, and the distance from it and from each other of the attendant spectra varies with the angle of incidence of the light.

The brilliance of this intermediate white image, representing no crystallographic face, becomes greater as the striation becomes finer, and when the width of the strip-faces the alternation of which forms the striæ becomes not very much greater than the longest wave-length of light, the theory of diffraction or bending of light-waves round sharp edges is in accordance with the supposition that the tangential plane acts as if it were a real face. Hence, the white image afforded by a finely striated face is absolutely useless for crystallographic purposes, in the



zone parallel to the striations. In the zone at right angles, however, the images are occasionally trustworthy, but it is infinitely more satisfactory to discard a crystal altogether which exhibits striation, or at any rate not to employ the angles in the zone in which it occurs as basal angles from which to calculate the crystal elements. If either of the two strip-series belong to a zone of intermediate situation the image properly belonging to the zone may often be detected and identified, when the zone is adjusted, by the fact that it passes through the centre of the field of the telescope, the other images being obliquely echeloned on either side above and below the horizontal spider-line. The degree of accuracy with which it may be allocated to the spider-lines, however, is rarely high, on account of blurring.

Thus striated faces are to be shunned by the crystallographer for the purposes of measurement, although they are so interesting from the structural point of view. In serious investigations the only safe course is to ignore such crystals entirely during the measurements, and to seek for crystals which are free from striation. It may happen that many crops of an artificial chemical preparation will have to be grown before one is obtained comprising crystals which are adequately free from striation.

**Vicinal Faces.**—The other type of multiple image to which special attention has to be called is observed when the face under examination is not the expected one, but is one of several closely-lying or "vicinal" faces replacing it. It may be that one image of the many constituting the ribbon-like series of multiple images already mentioned as afforded by an apparently distorted face vastly predominates over the others, this being characteristic of the vicinal faces of crystals belonging to the lower systems of symmetry; or it may be that three or four images, some or all of which are slightly out of the zone, appear instead of a single one, and they may either all be approximately of the same intensity, or, as more commonly happens, one image of the group may predominate largely in intensity, and cause the observer to take it for the image of a proper face of the crystal. This phenomenon of vicinal faces has been specially studied by Sir Henry Miers,<sup>1</sup> and his results published in the year 1903 are both curious and highly instructive, as affording an insight into the structural processes occurring during the growth of a crystal. The author also had frequent occasion to observe the phenomenon during his researches on the simple and double sulphates and selenates, and precautions had been taken from the beginning of the work in the year 1890 to avoid all measurements in which the phenomenon was involved.

A study of a growing crystal of potash alum (cubic, class 30, octahedron the predominating form; see Fig. 122 on Plate II. facing page 154), led Miers to the observation that the images from the various faces continually altered their positions, that the angle between the adjacent faces was never the theoretical angle of the regular octahedron, and that the faces usually yielded multiple images lying very close together. The latter were subsequently found to be three in number, of which one was often very much brighter than the others,

<sup>1</sup> *Phil. Trans.*, A, 1903, vol. 202, p. 459.

due to the octahedron face being replaced by the facets of a very flat triakis octahedron, of which one face largely predominated over the others. The three images frequently changed their positions, the lines of movement being inclined at  $120^\circ$  to each other, but the movement did not occur continuously, but suddenly at intervals. It was very uncertain, however, whether the forms produced could be expressed by any rational indices, even by very high numbers. The angles of the vicinal faces varied at different times from the true octahedron face by  $2'$  to  $30'$ . Similar observations were made in the cases of sodium chlorate (cubic, class 28) and the sulphates of magnesium and zinc (rhombic). In the case of zinc sulphate, the primary prism faces varied from  $91^\circ 6'$  to  $91^\circ 15'$ , due to the production of various vicinal faces instead of the true primary prism  $\{110\}$ . In the case of magnesium sulphate, similar variations of  $20'$  were observed. Hence with crystals of comparatively low symmetry the mean of a number of measurements may give a result very far from the truth. In the cubic system the mean may give the correct result, as the vicinal faces follow the high symmetry; but in the case of a rhombic prism each face will, from the lower symmetry, be replaced by one vicinal plane only, and the prism angle afforded may be considerably too large or too small.

Miers further showed that the vicinal planes follow certain specific well-defined zones only, and that to replace primary faces by vicinal planes is to replace planes of the greatest possible reticular density, referring to the space-lattice structure of the crystal (to be dealt with in Part II.), by planes of the least possible reticular density. Moreover, among the causes of the phenomenon, change of concentration during crystallisation appeared to be most actively influential. Hence, Miers suggests as the explanation, that the escape of the largely preponderating number of water molecules, during deposition of the relatively much fewer salt molecules from the only slightly supersaturated solution, causes the shower of solid salt particles to fall in a loosely packed condition, and if they be laid down as plane layers thus widely spaced, the plane at any moment is a vicinal face, rather than the primary face itself in which the structural units are packed in their closest order.

It may be of use to other workers to indicate briefly the precautions taken by the author to avoid the phenomenon investigated by Miers. Fortunately, even if the precautions had not been taken, the author's results would not have been affected for two reasons; firstly, because the real differences of angle between the various members of the isomorphous series, either the simple rhombic sulphates and selenates or the monoclinic double salts, although very small, as shown in the previous section of this chapter, were still much larger (in the maximum  $1^\circ 21'$  and  $2^\circ 28'$  respectively in the two series) than the angular differences observed between the vicinal faces and the primary planes which they replaced; and secondly, because the whole of such an isomorphous series of salts is similarly affected by the phenomenon, so that comparisons are absolutely valid.

Ever since the commencement of the work in the year 1890 great

efforts, invariably with successful results, were made to eliminate vicinal faces. Of each salt a large number of crops, often exceeding a hundred, were prepared, with all the precautions described in Chapter II. against disturbance during crystallisation. The result was that some half-dozen crops of each salt were obtained, in which an adequate number of small crystals were discovered of so perfect a character as to show no sign of vicinal faces, the primary planes themselves being developed at the theoretical angles. These crystals were, as a rule, much smaller than those employed by Miers, and had been deposited under conditions of extreme quietude in a room set apart for the purpose, and from solutions screened from all rapid change of temperature.

One example may be given with advantage, as illustrative of the kind of experience which may be expected. It will be taken from the monoclinic double sulphate and selenate series,  $R_2M\left(\begin{smallmatrix} S \\ Se \end{smallmatrix} O_4\right)_2 \cdot 6H_2O$ , of

which ammonium magnesium sulphate, described in detail as an example of monoclinic symmetry in Chapter XVII., is a member. The crystals of this series generally show striation of the faces of the basal plane  $c = \{001\}$  and the primary prism  $p = \{110\}$ , parallel to the symmetry plane  $b = \{010\}$ , due to the formation of vicinal faces instead of the true  $c$  and  $p$  faces. The directions will be clear from the shading in Fig. 329.

In the case of the  $c$ -faces, when the zone  $[bqc]$  is adjusted parallel to the axis of the goniometer, two images of the Websky signal, separated by about  $20'$ , usually predominate very markedly in the bundle, symmetrically arranged to the symmetry plane, that is, about  $10'$  on each side of the position for a true  $c$ -image. The position of the true  $c$ -plane is precisely indicated by the excellence of the reflections afforded by the faces of  $q = \{011\}$ , which are generally perfect on well-formed crystals, as well as by the faces of the clino-pinakoid  $b = \{010\}$ , which were also uniformly good, and yielded perfect signal-images.

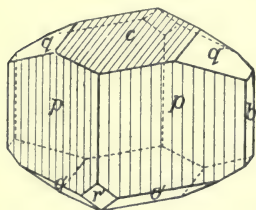


FIG. 329.—Striated Crystal of Ammonium Magnesium Sulphate.

These two forms are peculiarly free from the vicinal-face phenomenon, so that not only do vicinal faces follow specific zones, as observed by Miers, but they affect only specific forms in those zones. When the zone  $[cr']$  is adjusted the  $c$ -images, whether those of the true plane or of the vicinal faces, are invariably trustworthy in the case of well-formed crystals. For even if vicinal images, they are vertically over each other and do not affect the horizontal measurement. But even besides this frequent excellence

of the  $q$ - and  $b$ -faces, the author eventually succeeded in preparing crystals which showed no trace of the vicinal faces at all, but only those of the true  $c$ - and  $p$ -planes.

The kind of thing that was observed with respect to the  $p$ -faces on the usual type of fairly good crystal which does show vicinal faces was as follows. The image corresponding exactly to  $\{110\}$  was always present, but generally in a bundle of which the two extremes were not



symmetrical (naturally from the nature of the symmetry) to it, that is, it was not the central image of the bundle. Also it was not usually the brightest, the latter being sometimes on one side and sometimes on the other. Perfect  $p$ -images from the true  $p$ -plane were, however, afforded in the cases of the few specially excellent crystals referred to above, and the values obtained with them for the angle  $bp$  were always the same, within the usual limit of  $1'$  or  $2'$  for even the very best of crystal faces.

The interesting fact was also observed that the true position of the  $c$ - and  $p$ -faces is always clearly indicated by a particularly trustworthy image being afforded whenever the crystal has grown with one of these planes in contact with the flat bottom of the crystallising vessel. Such contact faces are always marked with contour lines, as shown in Fig. 330

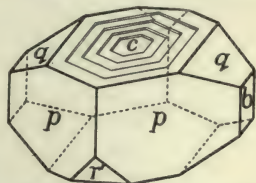


Fig. 330.—Crystal of Ammonium Zinc Sulphate, showing Contoured Contact Face.

in the case of a broad  $c$ -face of one of the crystals of ammonium zinc sulphate, which had been during growth the lower one in contact with the bottom of the dish. These contours are due to a lifting up of the crystal during growth, with eventual production of a hollow pyramid, arranged in steps, owing to the central part of the face not being in contact with more than a film of the saturated solution, whilst the margin is in contact with ample solution and has full facility for the deposition of the shower of solid salt particles. A series of shallow steps are thus produced, the horizontal strip-like surfaces of which, bounded by contour lines resembling etched figures, are parallel to the plane undergoing growth. Now the interesting point is that the whole of these contour strips, which together make up the crystal face, afford a single image of the signal, and accurately in the correct position for a true  $c$ - or  $p$ -face. For in all such cases the values for the angles  $cq$  or  $bp$  are found to be identical with the values derived from the very few exceptionally perfect crystals, free from vicinal faces, used in the actual measurements. It would thus appear that the favourable conditions for the formation of vicinal faces, that is, for the deposition of the salt particles in a loosely packed state, are not presented at the plane of contact with the crystallising vessel. Hence such contact-plane faces may be used to obtain trustworthy images in the event of absolutely perfect crystals not being eventually obtained.

**Special Goniometer for the Study of Growing Crystals.**—For the study of the vicinal faces of a growing crystal Miers employed a special goniometer, which is shown in Fig. 331.

This instrument is essentially a horizontal-circle goniometer with all the usual adjustments, but with the crystal-holder and the adjusting movements suspended below the circle instead of being placed above, so that the crystal may dip into the glass cell  $a$  containing the mother liquor. A cell of rectangular form is seen in position in Fig. 331 and is usually employed, but an alternative one of cylindrical shape with parallel plate-glass front is occasionally preferable, and is shown in Fig. 332, along with an adjustable table for it, which is often very useful. The sides or front of the cell

through which the light rays pass are in any case formed of truly parallel plate-glass, and the cell itself is placed on an adjustable stand *b* at the height of the telescope *c* and collimator *d*. The divided circle *e* moves over a circular plate *f* which carries the verniers, and which is rigidly carried by two vertical columns *g* (hollowed longitudinally to confer lightness). The collimator is also carried by one of these columns, but the telescope is carried at the lower end of a stout counterpoised arm *h* suspended from a thick plate *i* below the vernier plate, which with the axial boss *j* and the counterpoise *l* which is solid with it is capable of

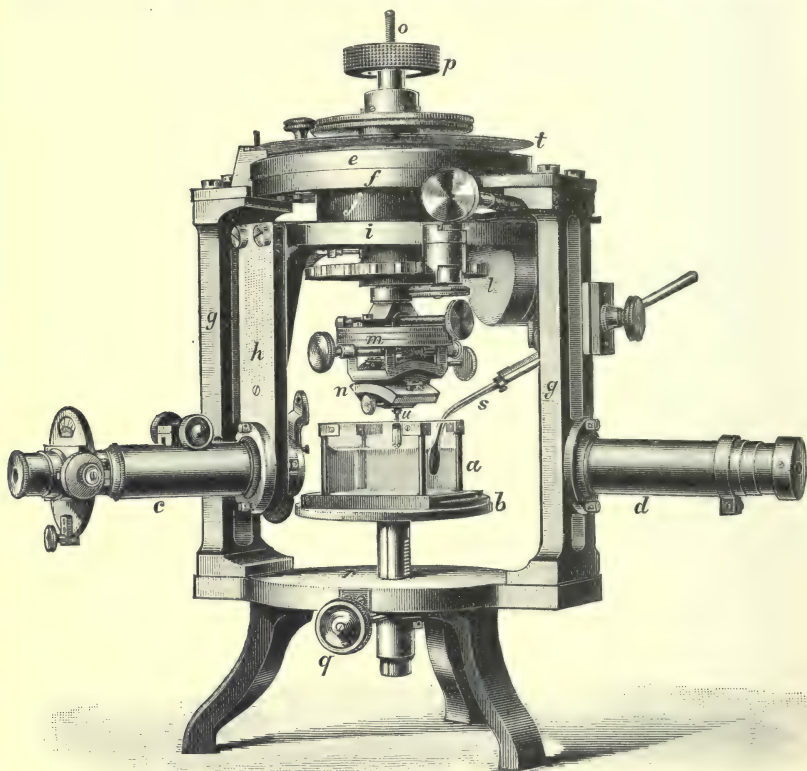


FIG. 331.—Miers Suspended Goniometer.

rotation about the axis of the instrument, outside the fixed cone, and of being clamped in any desired position. The centring apparatus *m* and adjusting movements *n* are of the usual goniometrical kind, and the inner steel axis *o* from which they are suspended can be raised or lowered by means of the milled head *p* at the top of the instrument. The adjustment for height of the cell table *b* is effected by means of the screw *g* seen in front below the raised base *r* of the instrument. The temperature of the liquid is read by the thermometer *s* with conveniently bent stem shown in the figure. The trough is arranged so that one of its faces is perpendicular to the collimator, a brass guide on the little supporting table ensuring this adjustment.

The crystal-holder, or the circle, or the telescope may be independently rotated round the fixed axis of the goniometer, and any two of these parts may be coupled together in rigid connection at will, a metal disc *t* above the circle-plate and to which

the clamping is effected acting as the connecting link. The goniometer is thus rendered equally suitable for use as a spectrometer for refractive index determinations. The telescope and collimator are each fitted in collars which may be adjusted by means of three screws, and the telescope is provided with rack-and-pinion adjustment, so that when it is converted into a microscope by moving into position the usual viewing lens in front of the objective the crystal may be properly focussed when immersed in liquids of different refractive indices.

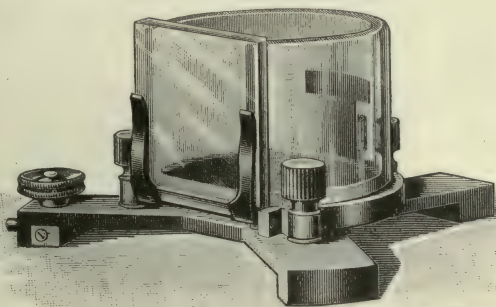


FIG. 332.—Immersion Cell for Use with Suspended Goniometer.

The crystal is held in a little clip of platinum foil, which in turn is held by a screw-clip holder *u* fixed in the usual manner at the base of the adjusting movements; in the course of the growth of the crystal in the mother liquor held in the dish the platinum becomes grown over and the crystal consequently very rigidly held.

For measuring the displacement of an image in any required direction within the field of view of the telescope a special eyepiece is provided, the plan of which will be gathered from Fig. 333. A similar one was adopted by the author on his cutting and grinding goniometer (Chapter XLIII.) with the kind permission of Sir Henry Miers. During the growth of a crystal the measurements can only be made in the adjusted zone, but variations of angle may be due to the displacement of a face out of the zone as well as in it. Suppose *O* to be the image of the collimator signal (a square one being particularly suitable for this work) as adjusted to the centre of the spider-lines; and suppose that during the growth of the crystal this image moves out of the adjusted zone *CC* to a position *P*. We require to measure the distance *OP* and the angle *POC*, which we may label  $\theta$ . To enable this to be achieved a third movable spider-line *MM* is provided, which is both rotatable and capable of movement transversely to its length in the focal plane by means of a micrometer screw *S*, this movement being registered by a drum-head divided into 100 parts. The movable wire and the micrometer is attached to a circular frame provided with milled edges by which it can be rotated about the centre *O*; the frame envelops a circular disc graduated so as to read directly to degrees, and the angle of rotation is read by means of a vernier *V* engraved on the inner bevelled side of an aperture cut in the frame, through which the scale on the fixed disc is viewed, which enables the readings to be made to minutes of arc. A toothed scale registers the number of complete turns of the micrometer screw. Hence, both the distance *OP* and the angle  $\theta$  can be directly measured. The movable disc and its spider-line can be clamped to the fixed disc in any position by means of the fixing screw *R* shown in Fig. 333 at the lower right-hand edge of the circular frame. This arrangement enables an image to be followed, whether its movement be as usual, in the zone itself along the horizontal spider-line, or out of the zone in some other direction, or either in or out of the zone but with the image rotated more or less out of the perpendicular.

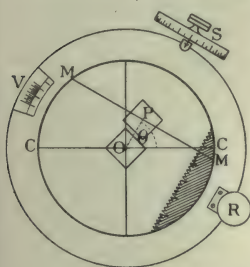


FIG. 333.  
Principle of Micrometric-  
Goniometric Eyepiece.

ment enables an image to be followed, whether its movement be as usual, in the zone itself along the horizontal spider-line, or out of the zone in some other direction, or either in or out of the zone but with the image rotated more or less out of the perpendicular.



For the purpose of measuring crystals immersed in the mother liquor, one face of the rectangular glass trough having been set automatically by means of the guide perpendicular to the collimator, the telescope is set perpendicular to the adjacent face of the trough by viewing the images of the crossed spider-lines reflected at its surface, by means of the light from a lamp placed beside the telescope and sent down the latter by reflection from a glass plate held obliquely before the eyepiece, the Becker fitting described on page 41, and illustrated in Fig. 24, serving admirably for this purpose.

Besides all ordinary purposes of goniometry this instrument can be used for measuring a crystal in a concentrated solution of its own substance (mother liquor) as above described; for observing the changes of form which a crystal experiences during growth; and for the measurement of deliquescent crystals, or such as are liable to alteration under ordinary atmospheric conditions, while immersed in oil or other suitable inert liquid. The action of solvents on crystals can also be studied by measuring them while immersed in acids or other solvents, and thus ascertaining the angles made by the etched-figure faces with the original crystal faces. The refractive indices of solid plates, prisms, or whole crystals can also be measured either by the method of total reflection or that of minimum deviation (both to be described in later chapters), by immersing them in suitable liquids; and the refractive indices of a liquid can be similarly measured by means of a plate or prism immersed in it. Further, the angles of isomorphous mixed crystals may be determined as the composition changes, by measuring a crystal while in the solution of another salt of the series, or measurements may be made of the enveloping crystal grown in such a solution upon the kernel of the original salt, in order to establish the relation between the shell and the kernel.

**The Measurement of Deliquescent Crystals.**—As above indicated, the goniometer shown in Fig. 331 may be used for the measurement of such crystals as are affected by the moisture of the air. The fine polish of a crystal face rapidly deteriorates on removal of the crystal from the desiccator in which it had been stored, when the substance is one having the well-known affinity and attractive force which many substances possess for water, either as a result of extreme solubility or of a still more active and truly chemical affinity for the elements of water. The crystal is immersed during the measurements in an inert liquid, such as benzene, carbon tetrachloride, or other suitable liquid, the index of refraction of which must be known with great precision.

A special apparatus, however, for conducting the measurements in the usual manner with the No. 2a goniometer, is supplied by Fuess with that instrument. Its construction will be clear from Fig. 334.

It consists of a glass vessel *a* fitted with two truly-plane plate-glass windows *b* opposite the usual positions of the collimator and telescope; the crystal can be enclosed in this desiccating chamber in an air-tight manner, while permitting some degree of adjustment of the crystal and providing a receptacle for a quantity of a desiccating agent such as calcium chloride or phosphoric anhydride. The ordinary crystal-holder is replaced by a special adjustable one, as the ordinary adjusting apparatus cannot be used, owing to the fact that an arm *c*, acting as a strong spring,

rigidly connects the top of the crystal chamber with the collimator tube. The arm is expanded at one end and bent round into the form of rather more than half a cylinder *d* so as to clutch the collimator, while the narrow end of the arm has a short slot and a somewhat wider hole, the former to pass over a steadying pin *e* and the latter to rest on a central knob *f*, both carried on the top of a little metal disc cemented to the indiarubber stopper *g* which closes the neck of the crystal chamber. The base of the latter is blown in and its central part is open, the channel *h* thus left around the middle part of the base serving for the reception of the

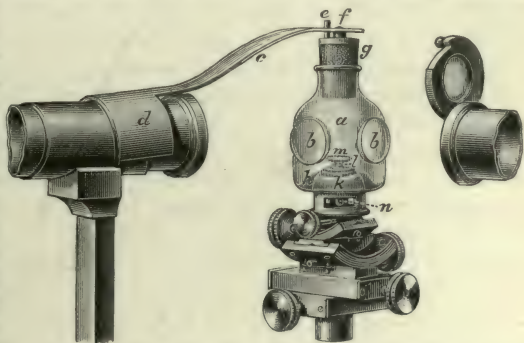


FIG. 334.—Apparatus for Use in the Measurement of Deliquescent Crystals.

desiccating material. The outside of the part blown in is ground to fit closely the upper spherical part *k* of the special crystal-holder, which consists of a hollow hemisphere mounted on a flat base, carrying below the peg for attachment in the hole at the top of the ordinary adjusting apparatus instead of the usual crystal-holder. The upper part of the hemisphere carries a little ball-and-socket joint *l*, the ball passing upwards into a little table *m* for the usual wax crystal-holding cone which projects through the opening into the chamber, and below into a short rod *n*, by which the adjustment of the crystal can be effected; the rod is manipulated by a little handle, perforated with a hole near one end to fit the rod, and to allow the insertion of which the lower part of the fitting above the base is open, the hemisphere being continued down on to the base in short columnar fashion merely at three equidistant places.

In using the apparatus, the chamber is first furnished with a little fresh dessicating substance, calcium chloride being usually most suitable; the crystal is mounted on the wax and the whole holder then placed in position on the adjusting apparatus of the goniometer. A trace of oil is smeared on the upper part of the little hemisphere and the chamber fitted with its ground part over it, the oil thus closing the lower part completely by rendering the fit air-tight. The stopper is then inserted above, and the arm-end placed over it, the other wide semi-tubular end, which is packed inside with cloth, being fitted over the collimator end, which it just grips, being rather more than half a cylinder. When this is effected the arm will be pressing the chamber tightly down on the hemisphere, and the peg of the stopper, which fits in the slot near the arm-end, prevents any rotation of the crystal chamber during the rotation of the circle and crystal, the oil lubrication between the hemisphere and the ground base of the chamber facilitating free rotation without any drag on the chamber. The adjustment of the two faces of a zone is then carried out with the aid of the key, a few approximations being required before the adjustment is perfect. Unfortunately, only a few closely-lying zones, sometimes only one, can be adjusted with the

same setting of the crystal, and every setting means opening the chamber to the air again.

The author has, consequently, not found this apparatus to be quite satisfactory in actual practice. It was subjected to a severe test during the work on the selenates of potassium, rubidium, and cæsium. These three salts are progressively deliquescent, following the order of the atomic weights and atomic numbers of the metals. Cæsium selenate is so highly deliquescent that the crystals eventually dissolve in moisture attracted from the air. The desiccating chamber was used when the measurements were being carried out on moist days, but it was found better in the cases of potassium and rubidium selenates to work only on very dry days, such as when an easterly or northerly wind was blowing, and to dispense with the special apparatus. It was found possible under those conditions to complete the measurements before the deliquescence had materially affected the brilliancy of the faces, other crystals having been previously well studied while the desiccating chamber was in position, so as to familiarise one with their character and thus facilitate the subsequent measurements. Even in the case of cæsium selenate this method, combined with the use of twice the usual number of crystals, so as only to carry out half the measurements on any one crystal and the remaining half on another, was found preferable to using the desiccating chamber, for the crystals proved to be as deliquescent as calcium chloride, and phosphoric anhydride became almost fully deliquesced before the operations could be begun. Still, in the cases of other deliquescent substances the apparatus might prove more serviceable.

For extreme cases of deliquescence, such as work which the author has on hand concerning the crystalline forms of the oxides of phosphorus,  $P_4O_6$ ,  $P_2O_4$ , and  $P_2O_5$ , it is preferable to enclose the whole goniometer and all accessories in a desiccating chamber, such as that (Fig. 528) which will be found described in Chapter XXXII., as used for specific gravity work on cæsium selenate. It is essentially an air-tight mahogany box, thoroughly well varnished inside and outside, and provided with plate-glass windows and two apertures closed with indiarubber gloves, in which the observer's hands are placed from outside during the manipulations. The goniometer and all the necessary accessories are enclosed overnight, along with phosphoric anhydride; one of the windows is removable for the purpose, and is immediately afterwards bolted on again. Indiarubber pads are fixed on both the side-cheeks and the window frame in order to ensure tight fitting. Next morning the air within is usually dry enough to enable successful measurements to be carried out, the only difficulty being the slight handicap incurred by the wearing of the gloves.

**Testing of the Goniometer Circle.**—Before concluding this chapter on goniometrical precautions and special difficulties in crystal measurement, it should be remarked that it goes almost without saying that the goniometer employed should be thoroughly tested as regards the accuracy of its circle, by repeating the measurements with the same



faces of a perfect crystal in various parts of the limb. If there be any difference amounting to a minute or two, such repetitions will be necessary throughout all investigations carried out with it, the mean of the various readings being accepted as nearest the truth. This, however, has never been necessary with the author's No. 2*a* and No. 1*a* Fuess instruments, nor with the larger Troughton and Simms goniometers, the division of the circle in each case having proved to be wonderfully accurate.

## CHAPTER XXV

### THE DRAWING OF CRYSTALS

ALL the drawings of crystals which have been given in the foregoing illustrations have been constructed accurately to scale (the pencilled construction lines other than the crystal axes having been eliminated after inking in the outlines) on a conventional plan, the so-called clinometric or clinographic projection, a slightly inclined form of "parallel perspective," according to which the eye is supposed to be removed to an infinite distance, so that parallel lines, instead of converging to a vanishing point as in ordinary perspective, are actually parallel in the drawing. The general appearance of the crystal, as regards foreshortening from back to front; is at the same time very faithfully reproduced, which confers a great advantage over the isometric projection. The method is now universally employed, and is the accepted mode of drawing crystals for publication in the *Zeitschrift für Krystallographie*.

The advantage will at once be obvious of a representation of a crystal on paper which, while correctly giving the impression taken in by the eye, assures that edges which are really parallel to each other shall still appear so in the drawing; for it is of the first importance to the detection and appreciation of the symmetry of a crystal to know which faces belong to the same zone, a fact which we have seen is indicated by the parallelism of their edges of intersection. Now the angle between the directions of two edges on different parts of a crystal is often so small that an inspection of a drawing in ordinary perspective would not inform us whether the edges were really parallel on the crystal or not, whereas on the plan adopted they are either parallel or not exactly according as they are drawn.

There is one further convention besides the parallelism of truly parallel lines and the back-to-front foreshortening, namely, that the eye is supposed to be raised somewhat above the horizontal plane, in order that something may be seen of the foreshortened upper faces of the crystal from above, and also somewhat moved to the right, in order to see the right-hand foreshortened side faces. The standard position, as afforded by the construction rules given on the next page but one, exhibits the crystal as if it were rotated  $18^{\circ} 26'$  to the left and inclined

9° 28' forwards. The designation "clinometric" or "clinographic" refers to this fact, and distinguishes the method from the orthometric or orthogonal projection, which represents the crystal as seen directly from above, as in a plan, or from the front, as in an elevation, a plane of symmetry being usually the plane of projection. Some examples of the orthogonal projection will be given in Chapter XXVII., for instance, Figs. 374 and 376.

In both the orthogonal and clinographic projections the light rays joining the eye and crystal coigns (solid angles, corners at which three or more edges meet) are all parallel, but in the former they are perpendicular to the plane of the paper on which the drawing is made, while in the latter they are inclined a few degrees out of the perpendicular to the paper.

The key to the whole drawing in clinographic projection is that of the crystallographic axes, which are first drawn in accordance with the rules of these conventions, and in agreement with the system of symmetry exhibited by the crystal. When once these are drawn, the crystal can be readily built up about them, for intercepts on these projected axes are proportional to the actual intercepts on the axes; and when the outline of the crystal is completed the axial scaffolding can be dispensed with, unless, as has frequently been the case in respect of the drawings in this book, it be considered desirable to indicate the positions of the axes by lines broken-and-dotted in order to distinguish them from the continuous lines indicating the front faces and from the dotted lines indicating the back faces. The pencilled auxiliary construction lines, however, may be erased after the inking-in of the crystal outline and axes. The recent development of "process reproduction" by photo-engraving has rendered it usually most convenient for the purpose of subsequent reproduction, which requires an exceedingly clear and clean drawing, that the construction shall be done on Bristol-board, a fine-surfaced dense cardboard particularly suitable for such drawings in Indian ink. If the drawing be that of an original crystal, and the results of the investigation are to be published, it should be made twice or three times the size it is required to appear, in order that the engraver may reduce it to the required size during his photographic reproduction, and so greatly enhance the neatness.

It must be remembered that the stereographic projection of a crystal—which will always have been drawn during the course of the measurements of the crystal angles and before the accurate drawing in clinographic projection is undertaken from the hand sketches of the crystal—is of the greatest help in constructing the clinographic projection. For it at once informs us which faces belong to any one and the same zone; and as all such interfacial edges are parallel, and parallel lines remain as such in the clinographic projection, these edges must be drawn parallel to each other, wherever they appear unreplaced by other forms. Moreover, the general direction of any zone oblique to the axial planes, and its relation to other zones, will be clearly apparent on the stereographic projection, and will enable confirmation to be obtained of the accuracy of drawing of the interfacial edges of the zone on the clinographic projection. Indeed, it is possible to determine the direc-



tions of the interfacial edges of such zones by the graphical methods of Penfield,<sup>1</sup> directly from the stereographic projection, when these directions are not already known by being parallel to the crystallographic axes. The student must, however, in any case be able to use the perfectly general and simple method of intersections described in this chapter, and can then with great advantage confirm the accuracy of the construction by reference to the stereographic projection.

**Rules for constructing the Axes of a Cubic Crystal.**—For all classes of crystals the axes have first to be constructed as for a cubic crystal, and then, when the latter is other than cubic, modified accordingly. Hence the construction of the cubic axes is of the first importance to the drawing of crystals, and it embodies all the various conventions which have been referred to. It is shown in Fig. 335, the method being the original one of Naumann, in the form recommended by von Groth, and as it is usually employed for crystal drawings published in the *Zeitschrift für Krystallographie*.

We first draw a horizontal line  $XX'$ , and a vertical line  $YY'$ , intersecting truly at right angles in the centre  $O$  of the drawing.  $XX'$  is then divided into 6 parts, and lines parallel to  $YY'$  are drawn through the two ends and through the second and fourth divisions. From  $X'$  a length  $X'P$  is set off downwards equal to one division, and  $P$  is joined to the centre  $O$  and the line produced to  $P'$ . The part  $AA'$  of this line  $PP'$  which is intercepted between the two parallel vertical lines drawn through the second and fourth divisions is the projection of the front-to-back horizontal axis of the crystal.

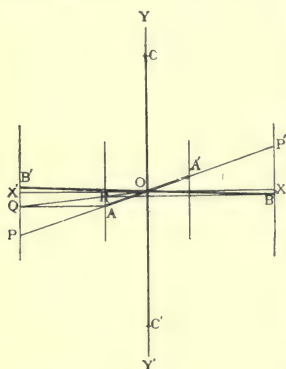


FIG. 335.  
Construction of Crystal Axes.

From  $A$  a line  $AQ$  is drawn parallel to  $XX'$ , and the point  $Q$  where it cuts the left-end vertical line is joined to the centre  $O$ , the line  $QO$  intersecting the second vertical line at  $R$ . From  $R$  another line  $RB$  is drawn parallel to  $XX'$ , meeting the right-hand vertical line at  $B$ .  $B$  is then joined to the centre  $O$  and the line  $BO$  produced to  $B'$ , equally on the other side of the centre.  $BB'$  is then the projection of the right-to-left horizontal axis of the crystal.

To determine finally the proper length of the vertical axis,  $OC$  and  $OC'$  are each made equal to  $OP$ .

As the cubic axes have to be drawn in the first instance, in the case of every crystal drawing, it saves much labour in their construction to have a permanent three-armed ruler or "templet" constructed for them once for all. By graduating each of the axial edges with a convenient scale, the larger units of which in each case are the unit lengths of the cubic axes as determined in Fig. 335, and the smaller units tenths of these, every five-tenths being emphasised by giving it an intermediate length, it is possible not only at once to mark off on the ruled axes the points corresponding to unit lengths and to twice and three times the unit lengths of the cubic axes, but also to mark off the proper lengths of the axes when the crystal is tetragonal or rhombic, the directions

<sup>1</sup> *Amer. Journ. of Science*, 1901, 11, 1 and 115; also 1902, 14, 249.

of the axes in these systems being equally rectangular and coincident with the cubic ones but the lengths differing. A three-limbed ruler of this nature may be constructed on these principles out of a single piece of thick sheet brass, the edges bearing the graduations being bevelled and perfectly straight. But the author finds one of the form shown (one quarter the real linear size) in Fig. 336 to be even more convenient. It has the advantage that both limbs of each axis are included, so that they can at once be ruled in and their lengths marked off. More-

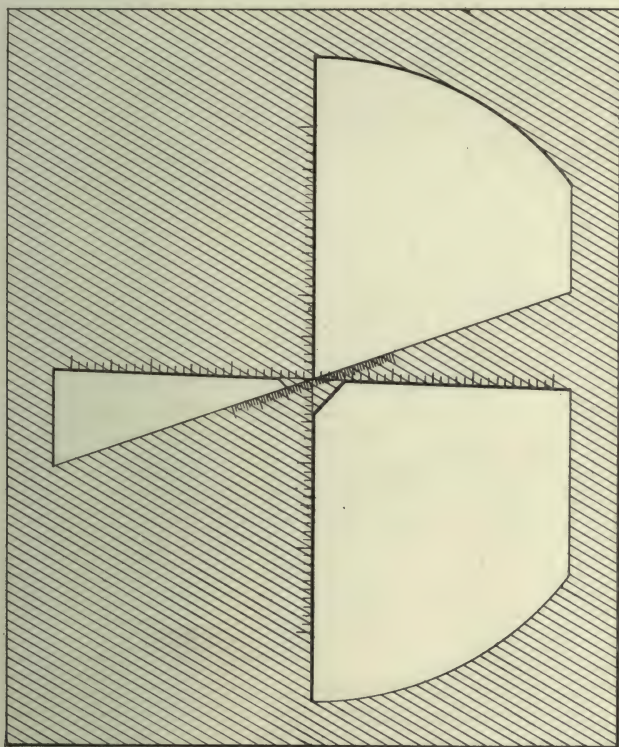


FIG. 336.—Templet for Drawing Crystal Axes.

over, it is by no means necessary to go to the expense of having it constructed of metal, although naturally it is then more durable and the edges are less likely to become damaged. The ordinary full-sized sheet ( $15\frac{1}{4}$  by  $12\frac{1}{2}$  inches) of the stoutest Bristol-board serves admirably, and enables three unit lengths to be graduated along each semi-axis from the centre outwards, on the same scale as that which has been used for all the original drawings for the illustrations in this book.

**The Drawing of Cubic Crystals.**—The form of the *octahedron* {111} is at once given by joining the ends of the axes to each other, as shown in Fig. 337, those edges actually visible in front and at the sides being

drawn in prominent but not too thick continuous lines, and those edges which are hidden from the eye if the crystal be opaque, behind the crystal, and which even in the clearest transparent crystal would be distorted by refraction if visible, are drawn in dotted thinner lines.

The **cube**  $\{100\}$  is obviously obtained as in Fig. 338, by drawing lines

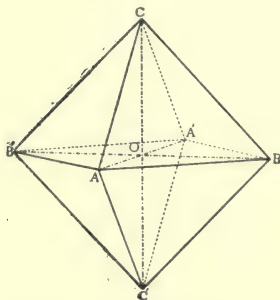


FIG. 337.  
Construction of Octahedron  $\{111\}$ .

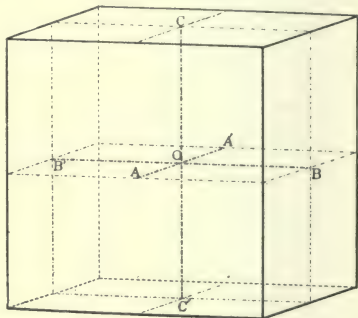


FIG. 338.—Construction of Cube  $\{100\}$ .

parallel to the axes and of the same length, in such a manner that the 6 ends of the axes are the centres of the six parallelograms representing the sides.

The edges of practically all other forms are constructed on the general principle of **finding the intersection of the two planes corresponding to the pair of faces meeting in each particular edge, the two planes being simply constructed by joining points on the axes corresponding to their intercepts.** The drawing of each of the principal forms of the cubic system will now be given, including the combination exhibited by the garnet crystal practically worked through in Chapter XI.; and this section will be concluded by the drawing of the somewhat more complicated combination of cubic forms, including one of a lower order of symmetry than the holohedral class 32, exhibited by the crystal of cobaltite also discussed in Chapter XI.

To obtain the direction of the edge between any two faces, we have first to convert their indices to intercepts, by the method given in Chapter V., page 78, to mark off along the three axes (assuming all three to be intercepted) the lengths corresponding to these intercepts for each of the two faces, and to join the three points in each case so as to obtain a representation of the facial plane; these two planes will then frequently meet or intercept each other at two points (usually an intersection and a point of contact), and the line joining these points is the direction of the edge between the two faces. In the not uncommon event, however, of the two planes as thus drawn only meeting at one point, one of them must be moved inwards parallel to itself until it touches the other at another point, conveniently the end of another axis, when it will intercept that other at a second point instead of merely touching at the first point referred to. We can always move the planes parallel to themselves until a convenient intersection of the two is obtained. Moreover, the direction of the edge afforded by the line of intersection is not necessarily actually the representation



of the edge itself; this latter may be drawn wherever it is required, parallel to the indicated direction.

These few simple general rules practically cover the construction of all crystals, even the most complicated.

The **rhombic dodecahedron**  $\{110\}$  affords a simple instance of the procedure by the method of intersections.

Each of the four front faces, meeting in an apex at A, intersects the axial plane BOC, Fig. 339, in one of the 4 thin broken-and-dotted lines DE, EF, FG, GD, which have been drawn parallel to the axes  $BB'$  and  $CC'$  through the ends of those axes. Obviously, therefore, the faces intersect each other in pairs at the corners D, E, F, G. As each corner is thus common to the planes of the two adjacent faces it must be a point on the edge between them, a second point being the apex A. The directions of the edges are therefore obtained by joining A to D, E, F, G respectively. The directions of the edges of the four similar back faces terminating at  $A'$  are in the same manner obtained by joining  $A'$  to the four corners. The other edges on the crystal are all parallel to these same directions already drawn, for every face of the rhombic dodecahedron is a regular rhombus and not merely a parallelogram. We draw, therefore, all the remaining edges from the ends of the axes  $BB'$  and  $CC'$  parallel to the proper edges terminating at A, as shown in the figure, and these lines will determine

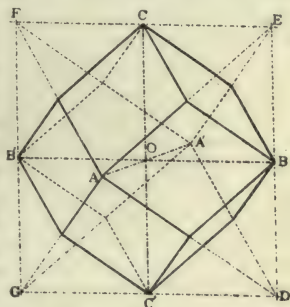


FIG. 339.—Construction of Rhombic Dodecahedron  $\{110\}$ .

the correct lengths of the original edges terminating at A, as well as of those terminating at  $A'$ , the directions of which only were given by joining A or  $A'$  to the corners. The back faces are, of course, to be drawn in broken or dotted lines.

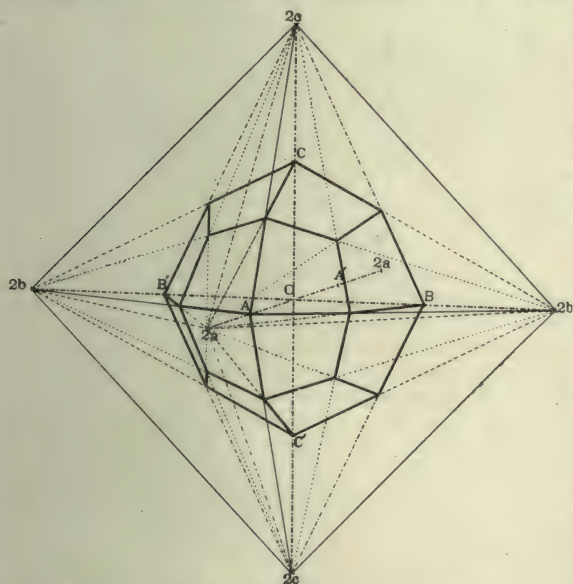


FIG. 340.—Construction of Icositetrahedron  $\{211\}$ .

The **icositetrahedron** can be readily drawn on the same principle, and it will next be shown in Fig. 340 how that represented by the indices  $\{211\}$  is drawn, the commonest form of this solid, that which is exhibited by the garnet crystal dealt with in Chapter XI.

We commence as usual by drawing in the axes by ruling from the templet; they are shown in the strong broken-and-dotted lines in Fig. 340, and two unit lengths are

required of each, unit lengths being marked off at A and A', B and B', C and C', and the double lengths at  $2a$ ,  $2b$  and  $2c$ . The 3 planes corresponding to the 3 faces of each octant are then drawn in, by joining their intercepts on the proper 3 semi-axes, and their intersections give the directions of the icositetrahedron edges. Taking the upper right octant as an example, the intercepts corresponding to the 3 faces (211), (121), and (112) (for the indices see Fig. 98, page 152) are respectively  $a : 2b : 2c$ ,  $2a : b : 2c$ , and  $2a : 2b : c$ . For the face (211) the points marking in front the unit length of  $a$  (namely A),  $2b$  to the right, and  $2c$  above, are joined, forming the triangle shown in thin continuous line in Fig. 340; for the face (121) the points marking  $2a$  in front, unit length of  $b$  (that is, B), and  $2c$  above are joined, forming the triangle shown in thin broken-and-dotted lines, and for (112) the points  $2a$ ,  $2b$ , and unit length of  $c$  (that is, C) are joined, forming the triangle shown in broken lines in the figure. Each pair of these triangles intersect at one point and touch one another at a second, the latter being  $2a$ ,  $2b$ , or  $2c$ ; and the line joining these two points, drawn dotted, is the direction of the edge between the two icositetrahedron faces corresponding to the two triangles, the three edges thus found being those which meet in the centre of the octant. The parts of the dotted junction lines which represent the actual edges on the crystal are drawn in bold continuous line, as being visible edges in front. The other edges forming the intersection of the three faces of this octant with those of the adjacent ones are actually parts of the sides of the triangles representing the planes themselves, as will be obvious when we have treated the other three front octants in the same manner, in order to get the three centrally converging edges of each of these octants, for it will be clear that the parts of the triangles in question, forming the other edges of the icositetrahedron, are each common to a pair of faces of the two adjacent octants the separation of which they mark, and are thus the lines of intersection, or edges, of those faces. Hence, the whole construction for the front half of the icositetrahedron is afforded by the four sets of three triangles. The back half may, of course, be similarly obtained, but as we are dealing with a perfectly symmetrical solid, and the figure is now getting complicated with numerous lines, it is perhaps simpler to make a tracing of the front half now drawn, and to reproduce it on the Bristol-board with the aid of a tracing stylus and a blacklead<sup>1</sup> interleaf, after rotating the tracing about the centre O (through which a pin is stuck) until the axes are again coincident, that is, for exactly  $180^\circ$ . As the figure is symmetrical the back faces are exactly like the front ones, but inverted, their outline being precisely that of the front half when the latter is turned round  $180^\circ$  in the plane of the paper. The whole figure of the icositetrahedron {211} shown in Fig. 98 (page 152) in Chapter X., in which the indices have also been inserted, was obtained from Fig. 340 in this manner by means of a tracing, care having been taken, by use of the set-squares or parallel ruler, that such edges as are parallel were made strictly so in the inking-in.

The same tracing was made use of for the drawing of the crystal of garnet, Fig. 132 (page 171), described in Chapter XI., and the small faces of the rhombic dodecahedron, marked  $d$  in the figure (the icositetrahedral faces being labelled  $i$ ) were inserted by the method of Fig. 339. For the icositetrahedron {211} directly replaces the edges of the rhombic dodecahedron, the faces of the two forms lying alternately in the same dodecahedral zone, so that the edges of intersection of the two forms are parallel to the edges of the latter form. The  $d$ -faces were given such a relative size as they possessed on the garnet itself, for we can, of course, move the edges parallel to themselves so as to represent faithfully the observed proportions, so long as the directions are those determined by the intersections.

The **trikis octahedron** may also be readily drawn on similar lines. The outline of the octahedron appears in this solid just as in the simple

<sup>1</sup> Pure graphite paper must be used; the carbon sheets used for duplicating type writing must be avoided, as they give lines which are ineradicable by india-rubber.

octahedron, but on each face a low triangular pyramid is erected. In Fig. 341 the construction of the triakis octahedron  $\{221\}$  is given.

The difference from the last construction is that here two of the three intercepts remain unity as for the octahedron, hence the fact that the octahedron edges persist, while the third is of double length, and for the three faces of any octant the three semi-axes become of double length in turn. The triangle representing the plane (221) (see Fig. 99, page 153, for indices) having intercepts  $a : b : 2c$ , is shown in continuous fine line, that for the face (212), with intercepts  $a : 2b : c$ , is drawn in thin broken-and-dotted line, and that for the third face (122), having intercepts  $2a : b : c$ , is given in ordinary broken line, and corresponding types of line are given for the 3 triangles of each of the other 3 front octants.

The two points where each pair of triangles representing the planes of adjacent faces meet and intersect give, when joined (by dotted lines in Fig. 341), the direction of the edge between the faces. One of these two points in each case is a point of intersection P and the other is a point of meeting at the end of an axis. The whole figure of the front half of the crystal thus obtained is drawn in strong lines, the part of each dotted intersection line which actually corresponds to the edge between the two faces in each case, and which therefore requires to be

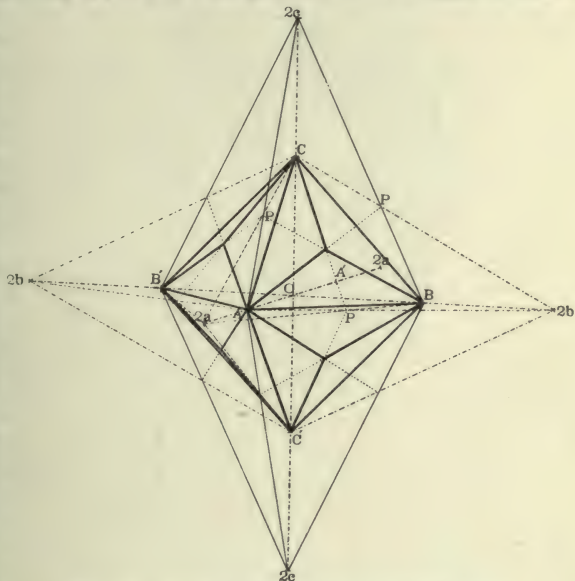


FIG. 341.—Construction of Triakis Octahedron  $\{221\}$ .

thus drawn in strong continuous line, being quite obvious. The illustration of the triakis octahedron given in Fig. 99 (page 153), Chapter X., accompanying the description of the form, was obtained by preparing a tracing of the crystal outline from this Fig. 341, and subsequently transferring it to Bristol-board with the aid of the tracing stylus and the blacklead interleaf, and the back half also given in Fig. 99 was obtained by rotating the tracing paper for  $180^\circ$  about a pin stuck through the centre O and again tracing from the front half thus inverted, except the octahedron edges which were drawn directly, the usual precaution being taken to render all lines strictly parallel which should be so, during the inking-in, with the aid of set-squares. The indices for the front faces are also inserted in Fig. 99, so that the two figures together enable the whole construction to be followed without undue complication of either.

**Tetrakis Hexahedron.**—In the case of this solid the cube forms the main skeleton, with a tetragonal pyramid erected on each face. The construction of the tetrakis hexahedron  $\{210\}$  is shown in Fig. 342.

The plane representing each face is now parallel to one of the axes, it cuts another at unit length and the third at double that length. The axes, the unit lengths of



them, and the double unit lengths, are drawn and marked as in the two previous figures; and also the lines joining the points on the axes corresponding to the intercepts, indicating the various facial planes, are drawn in the same manner, but only such of them as are essential, by their actual intersection or meeting, to the determination of the directions of the crystal edges, in order not unduly to complicate the

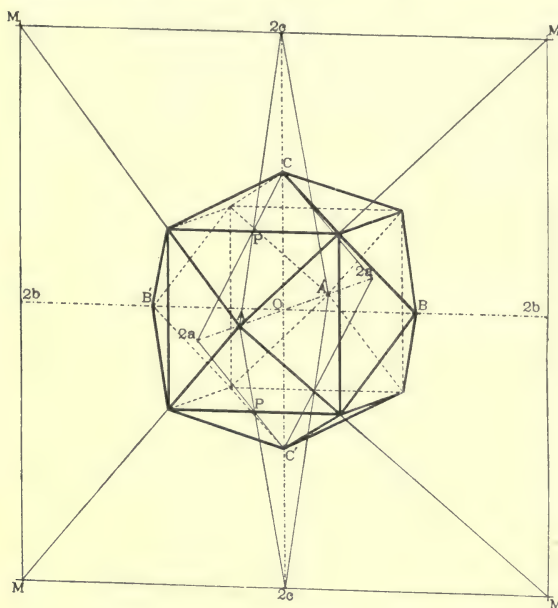


FIG. 342.—Construction of Tetrakis Hexahedron  $\{210\}$ .

figure. Thus P marks the point of intersection of two planes which determines the position of the cube edge in each case, parallel to the axis *b*, and M in each case marks one of the two meeting points of two of the front facial planes, the other being the end A of the axis *a*, so that the four lines AM are the directions of the four front pyramidal edges.

The outline of the crystal, as finally drawn in strong line, on the Bristol-board on which the construction was directly made for the purpose of this Fig. 342, was traced off on to tracing paper, and the tracing was transferred with the aid of the stylus and blacklead paper to another

piece of Bristol-board, in order to obtain Fig. 100 (page 153), the illustration of the tetrakis hexahedron which accompanies the description of the solid in Chapter X. The back half of the crystal was also traced in after rotating the tracing of the front half for  $180^\circ$ , and subsequently inked-in with thin broken lines. The indices are inserted in Fig. 100 for the front faces, which will enable the construction of the intersecting planes in Fig. 342 to be the more readily followed.

**Hexakis Octahedron.**—The construction for the  $\{321\}$  representative of this 48-sided crystal form, exhibiting the fullest type of cubic symmetry, and therefore the fullest of all possible symmetry, is given in Fig. 343. Although apparently complicated owing to the large number of faces, it is really quite simple. Only such construction lines as are essential are shown, in order not unnecessarily to involve the drawing.

The indices of the faces of the front half are given in Fig. 96 (page 151) of Chapter X., which was derived from the constructed Fig. 343 precisely as has just been described for the tetrakis hexahedron, and includes in the same way the back faces, inked-in with broken lines. It will be seen from Fig. 96 that the indices are all formed by the three figures 3, 2, and 1, and the intercepts consequently are always either 1,  $\frac{2}{3}$ , or 3. These lengths are, therefore, shown marked off along each of the three axes in Fig. 343, and every facial plane meets each of the axes at one of these three lengths. To construct every one of the 24 triangles representing the front facial

planes completely, by joining three of these points in each case, would produce a maze of lines, so only such of the junction lines as are really required to give the essential intersections or contacts for the determination of the directions of the interfacial edges are actually shown, although most of them were put in originally in pencil, but erased after the inking-in of the lines actually needed. For instance, the direction of the edge between the face  $(321)$ , the face which gives its indices to the form, and that below it,  $(32\bar{1})$ , is afforded by the intersection of the two planes having the corresponding intercepts  $a : \frac{2}{3}b : 3c$  in each case, the  $3c$ , however, being marked off along the

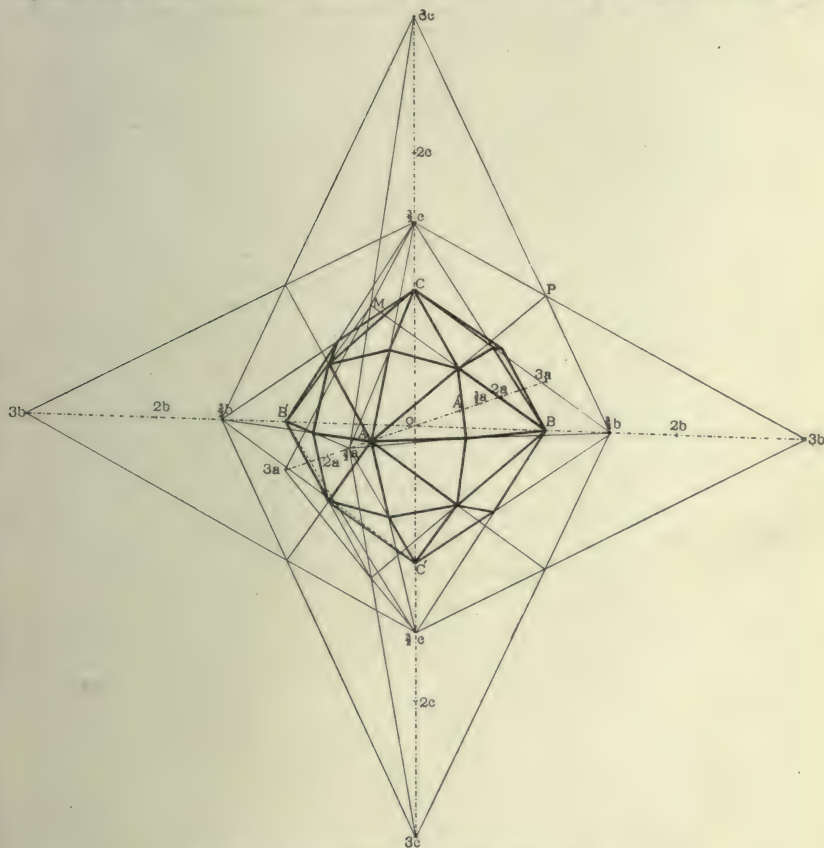


FIG. 743.—Construction of Hexakis Octahedron  $\{321\}$ .

positive upper half of the vertical axis in the former case, and along the lower negative half in the latter, the  $a$  and the  $\frac{2}{3}b$  being identically marked off along the positive halves of those axes. The line joining  $A$  and  $\frac{2}{3}b$  is thus common to the two triangles representing the planes, and is therefore the direction of the edge between the planes, the edge itself, subsequently inked-in strongly, being part of it. A similar process affords us all the other edges lying in the cube planes, thus, for instance, the line joining  $B$  and  $\frac{2}{3}a$  is the direction of the edge between the next pair of faces to the right  $(231)$  and  $(23\bar{1})$ , and the part of it which is the actual edge itself is determined by its intersection with the edge-direction between  $(321)$  and  $(32\bar{1})$  already found, being that part of the thin junction line which lies between  $B$  and this intersection, just as

the part of the junction line between A and the intersection is the actual edge between (321) and (32 $\bar{1}$ ). Again, to find the edge between the same form-indicating face (321) and that above it to the left, (312), the intercepts are respectively  $a : \frac{2}{3}b : 3c$  as before and  $a : 3b : \frac{2}{3}c$ ; the triangles formed by joining these intercepts have a common meeting point at A and a point of intersection at P (the intersection of the sides  $3b : \frac{2}{3}c$  and  $\frac{2}{3}b : 3c$ ). The line AP, therefore, is the direction of the required edge. The point in the middle of the octant, at which this edge, starting at A, terminates, and to which five other edges also radiate, is found by one further construction, say by that of the edge between (231) and (132); the intercepts are  $\frac{2}{3}a : b : 3c$  and  $3a : b : \frac{2}{3}c$ , and the two triangles formed by joining these intercepts have the point B in common and intersect at M, so that BM is the direction of the edge in question. Where AP and BM cut each other is, therefore, the radial point in the middle of the octant, and we can consequently draw in the two actual edges under discussion by thickening the parts of AP and BM starting at A and B respectively and terminating at this radial point. Moreover, we can also draw in at once the other four edges radiating to the same point, from C and from the three intermediate points between A, B, and C where the edges lying in the cube planes, already found, meet. In a similar manner the interfacial edges of the other three front octants can be drawn, the necessary triangle-sides being all given in thin lines in the figure, so that the process can be readily followed. The finished outline of the front half of the crystal thus obtained, as clearly marked by the thickened lines, was reproduced by the tracing process already fully described, in the Fig. 96 already alluded to, and the back faces inserted after the rotation of the tracing for exactly 180°.

To conclude the discussion of the drawing of cubic crystals an example of a **combination** will be taken, which includes not only the fully symmetrical forms of class 32 but also one selected from the classes of lower symmetry, a so-called hemihedral form. The example chosen is the crystal of **cobaltite** described and worked through practically in the latter half of Chapter XI. It comprises faces of the cube, octahedron, and the pentagonal dodecahedron {210} of class 30.

Its construction is shown in Fig. 344, only such structural lines being given as are essential to the determination of the directions of the various edges. Also, after having found by construction the direction of a single edge of any zone, the knowledge gained from the practical measurement of the crystal as to which faces and their interfacial edges belong to the same zone has been fully utilised, for such edges must always be parallel to each other. After the completion of the drawing of the front half of the crystal, a copy of its outline was traced for Fig. 134 (page 180) in Chapter XI. describing the work on this crystal; and the back half was subsequently inserted after the rotation of the tracing about the centre for 180°. The letters *c*, *o*, and *p* on the faces in Fig. 134 indicate which belong to the cube, octahedron, and pentagonal dodecahedron respectively. Fig. 116, page 163, representing the latter form with its indices, will be helpful.

Commencing with the front faces of the pentagonal dodecahedron (210) and (2 $\bar{1}$ 0), right and left of the front-central vertically elongated cube face which replaces the edge between them, it will be best at first to ignore the latter, and to draw in the two *p*-faces as if alone present. The direction of the edge between them is obviously that of the vertical axis, as both faces are parallel to that axis, the *c*-index of each being 0. The place where we shall draw this vertical edge may be left, however, until we have found the most convenient situation relatively to the determination of the edges between the *p*-faces and the adjacent *o*-faces. To proceed to find, for instance, the direction of the edge between (210), the right central *p*-face which gives its indices as symbol for the form, and the primary octahedron face (111) above it, we first join A,



B, and C to represent the plane (111), and then similarly draw in the plane (210), the intercepts of which are  $a : 2b : \infty c$ , by joining A to  $2b$ ; vertical lines parallel to axis  $c$  from A and from  $2b$  should be understood to represent the  $\infty$  value of  $c$ , but are not actually drawn as they are not wanted. This line A :  $2b$  representing the (210) plane, however, only touches the (111) triangle at A, so in order to get an intersection we must move one (either) of them parallel to itself in the direction of the other; the  $p$ -plane has been so moved nearer to the centre O until it has intercepted the  $b$ -axis at B, which is then common to the two planes instead of A, the  $a$ -axis being intercepted at a point L, half-way between A and O. From L a line parallel to the vertical axis is drawn, cutting the octahedron edge AC at P. P is thus a second point

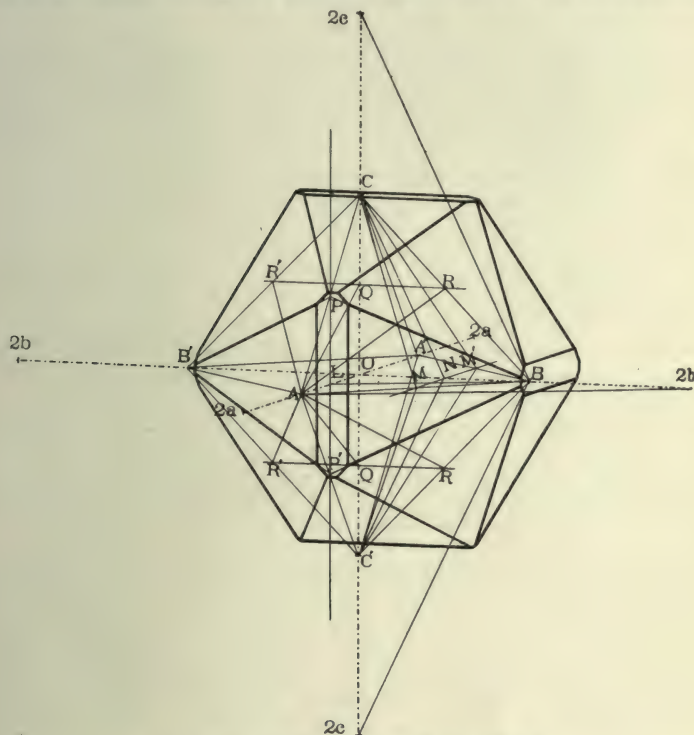


FIG. 344.—Construction of Crystal of Cobaltite.

common to the octahedron and the pentagonal dodecahedron, and if we join it to the other common point B we have the direction of the required edge. The edge between the same (210) face and the  $o$ -face below it, (11 $\bar{1}$ ), is similarly along the direction BP', and the edges on the left side of the centre, between (2 $\bar{1}$ 0) and the upper and lower left  $o$ -faces are B'P and B'P'. The edge between the upper right  $o$ -face (111) and the  $p$ -face to the right of it (021) is determined in like manner, by constructing the plane (021) having intercepts  $\infty : b : 2c$ , that is, by joining B and  $2c$ , and then moving it parallel to itself until it cuts the  $c$ -axis at C, so as to make this a common point instead of B, when it will also cut the  $b$ -axis at N, half-way between O and B. Through N we draw a line parallel to the axis  $a$ , as the plane (021) is always parallel to that axis, and where this line cuts the octahedron edge AB, namely at M, will be the second point on the line of direction of the required edge CM. This line CM is not the edge itself, but

only its direction, but we can move it parallel to itself until it occupies the position actually observed on the crystal, namely, so as to form a common apex at B with the two edges of the face (210). The corresponding lower edge between the right lower *o*-face and the lower *p*-face to the right of the latter is similarly parallel to C'M. Further, the direction of the two other edges bounding these right-hand *p*-faces on the extreme right of the figure, between them and the upper and lower right back *o*-face are also given by CM' and C'M', and they can be drawn in eventually so as to meet the *o*-faces at the apex in each case as shown in the drawing, and as they really appeared on the crystal itself. But before actually drawing them in it is advisable to construct the edges between the *o*-faces and the upper central and lower central *p*-faces, so as to get the complete shape of both sets of faces, and to determine where the upper and lower apices on each side come. We can, however, at once utilise our knowledge of the directions CM' and C'M' in drawing in the two edges on the extreme left of the figure, meeting at B', for these are parallel to the two edges on the extreme right and therefore their directions are equally given by CM' and C'M'. To determine the upper and lower front *p*-edges, and incidentally the upper and lower apices, we proceed as follows. The upper central *p*-face is (102), making the intercepts  $2a : \infty : c$ , so we join  $2a$  and  $c$ , or, in order to get 2 points of intersection with the octahedron face (111) or ( $\bar{1}\bar{1}\bar{1}$ ), draw AQ parallel to the line joining  $2a$  and  $c$ . On drawing through Q a line RQR' parallel to the axis  $b$ , as (102) is parallel to that axis, we find that it cuts the octahedron edges at R and R'. Joining these respectively to the second point of the intersection, the lines AR and AR' are the directions of the edges *o* : *p* required, all four of which are drawn radiating (two from each) from P or P'. These edges meet at their upper and lower ends those of the *o*-faces radiating from B, thus determining the apices from which the extreme right *p*-edges can be drawn parallel to CM' and C'M'. The top and bottom lines of the figure are then obtained by joining, parallel to the axis  $b$ , the two top and two bottom apices.

This completes the figure as regards the *o*- and *p*-faces, and the narrow cube faces can then be readily inserted, the long edges being parallel to the three axes respectively, as are also the short terminal edges, while the inclined edges between the latter and the long edges are parallel to the ordinary octahedron edges. These cube faces are given the relative size in the drawing which they actually exhibited on the crystal.

As regards the insertion of the back faces in Fig. 134, after the transfer of the front faces from the tracing of the boldly drawn outline of Fig. 344, by rotation of the tracing for  $180^\circ$ , it will be obvious that the centre of rotation is not O, but the actual centre of the hexagonal marginal outline. For owing to the movement of the *p*-planes parallel to themselves O no longer remains the centre, as it does in the simpler cases previously considered, in which the intersections of the various pairs of planes corresponding to adjacent faces were obtained without any such parallel movement being required.

The drawing might have been made, however, so as to retain O as centre, by moving the octahedron planes outwards parallel to themselves, instead of moving the *p*-faces inwards, in order to get their intersection. But the course adopted was taken purposely, in order to emphasise the fact that the directions of the edges are equally well afforded by either course, and that it is these **directions** which are determined, and not necessarily the actual positions or relative lengths of the edges; the latter may be drawn anywhere, and of any length, parallel to the indicated direction, so as to reproduce faithfully the general appearance and relative prominence of forms of the crystal.

**Tetragonal and Rhombic Axes.**—When the crystal belongs to the tetragonal or rhombic system, in both of which the axes are still rectangular, the only difference introduced in the drawing of the axes is as regards their relative lengths, the construction itself being exactly the

same as for the cubic system. In the case of a tetragonal crystal the two horizontal axes  $a$  and  $b$  are allowed to remain as if for a cubic crystal, but the vertical  $c$ -axis has to be given its proper length, corresponding to the axial ratio  $c : a$ . Hence, after drawing in the cubic axes from the templet, and marking off the unit lengths of  $a$  and  $b$ , we mark off  $OC$  and  $OC'$ , so that these lengths above and below the centre are each equal to the value of the ratio, as given directly by the scale along the templet edge. When the crystal is of rhombic symmetry, only the right-and-left horizontal axis  $b$  is allowed to remain of the normal cubic length, and the front and back parts of the  $a$ -axis as well as the upper and lower parts of the  $c$ -axis must be given their proper lengths, corresponding to the axial ratios  $a : b$  and  $c : b$  (where  $b = 1$ ), by marking off  $OA$  and  $OA'$ , as well as  $OC$  and  $OC'$ , with the aid of the scales along the  $a$ -edge and  $c$ -edge of the templet, equal to the values of  $a$  and  $c$  in the ratios.

If we join the ends of the axes we obtain, in the case of tetragonal axes, the primary tetragonal bipyramid of the first order  $\{111\}$ , as shown in Fig. 345, and in the case of rhombic axes the primary rhombic bipyramid  $\{111\}$ , as shown in Fig. 346. The axes in the case of Fig. 345 are those which have the relative values corresponding to the axial ratio  $a : c = 1 : 1.7771$  (the two horizontal axes being of unit length and the  $c$ -axis being 1.7771 times cubic unit length), being those of the typical tetragonal crystal of anatase which was worked through practically in Chapter XIII. The axes in Fig. 346 have the three different values  $a : b : c = 0.5287 : 1 : 0.9539$

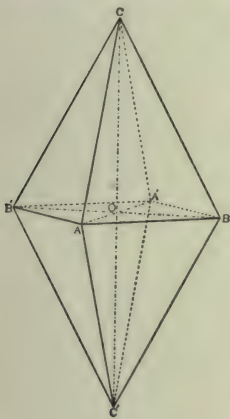


FIG. 345.

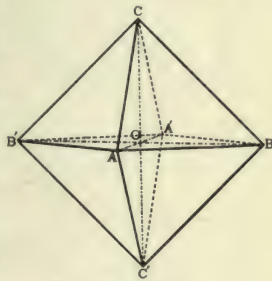


FIG. 346.

(that is, axis  $a$  is 0.5287 of cubic unit length, axis  $b$  is of unit length as in a cubic crystal, and axis  $c$  has the length 0.9539 of the cubic unit), corresponding to the axial ratio of the crystal of topaz worked through in Chapter XV. as an example of a rhombic crystal.

As they are possibly the best examples we could choose, the method of drawing tetragonal and rhombic crystals of some little complication will next be illustrated by going through the construction, stage by stage, of these typical crystals of anatase and topaz, which will fully illustrate the mode of drawing crystals belonging to these two rectangular systems.

Commencing first with *anatase*, the construction is shown in Fig. 347. The axial lengths correspond to the ratio above given and illustrated in Fig. 345, but the axes are produced so as to afford three unit lengths of  $a$  and of  $b$ , and two unit lengths of  $c$ , the forms present requiring these lengths in order to be able to mark off their intercepts. In the cases of  $a$  and  $b$  the unit lengths are also divided into thirds, as the intercepts on these axes in the case of one form are five-thirds of unit length.



The crystal was shown in Chapter XIII. to consist primarily of the two first order bipyramids  $z = \{113\}$  and  $r = \{335\}$ , the former occupying the two apices. Besides these prominent bipyramids, two others of the same order were also present as strips replacing the equatorial edges, namely  $p = \{111\}$  and  $s = \{221\}$ . The faces are not

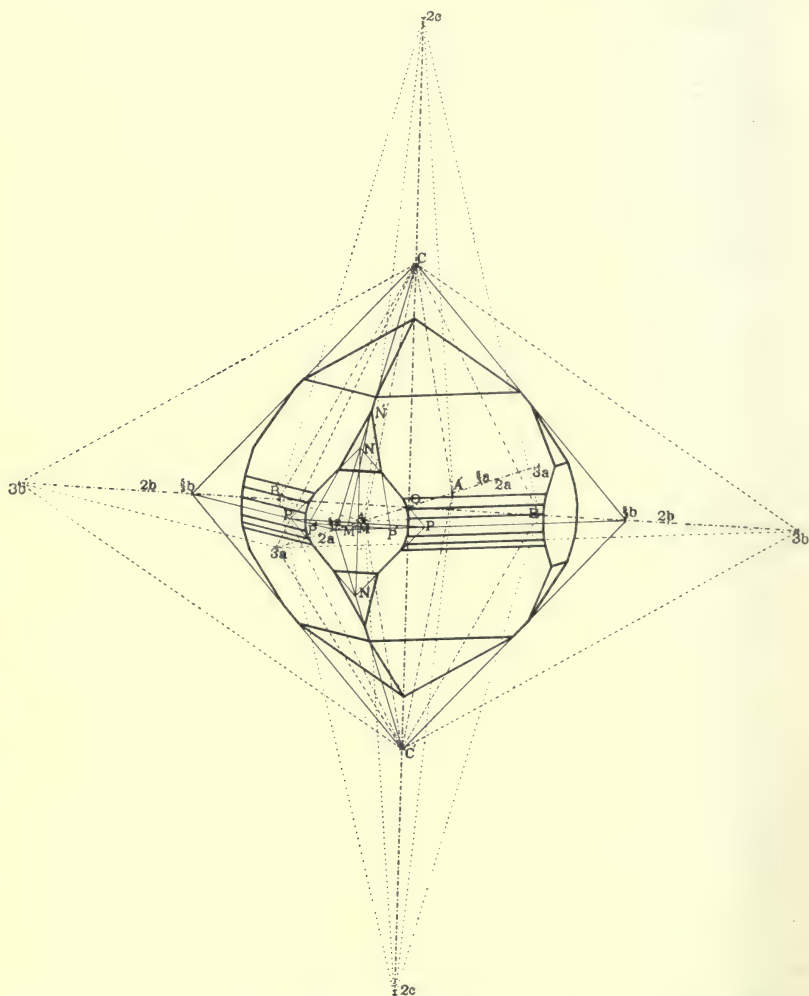


FIG. 347.—Construction of Crystal of Anatase.

lettered in Fig. 347, to save confusion with the construction letters; but the letters are given on Fig. 174 (page 208) of Chapter XIII., the illustration accompanying the description, which was reproduced by the tracing method from the original drawing for Fig. 347, the back faces being inserted (inked-in in broken lines) after the rotation of the tracing of the front half for  $180^\circ$  about the centre O.

The two prominent bipyramids were first drawn,  $r = \{335\}$  in thin continuous lines and  $z = \{113\}$  in broken lines. The intercepts corresponding to  $(335)$  are  $5a : 5b : 3c$ ,

or dividing by 3 all through  $\frac{5}{3}a : \frac{5}{3}b : c$ . The front half of the bipyramid was, therefore, obtained by joining the points on the three axes corresponding to these intercepts, which are clearly marked on them. It happens that only a very small part in the middle of each of the polar edges of this (continuous line) bipyramid actually exists on the crystal as an edge, owing to the extensive manner in which this form is modified and replaced by others. It is most convenient to take the form  $z = \{113\}$  next, having the intercepts  $3a : 3b : c$ . The front half of a bipyramid having these intercepts is the one drawn in the broken lines in Fig. 347, but it does not intersect or touch the steeper one already drawn. All we have to do, however, is to move it inwards parallel to itself, until it cuts off as much of the apices of the bipyramid  $r$  as it appeared to do on the actual crystal itself. That is, we draw the pyramidal terminations, upper and lower, parallel to the broken lines. The edges between  $r$  and  $z$  are parallel to the equatorial edges of all first order bipyramids, that is, to the lines joining unit  $a$  and  $b$  intercepts. Tackling then the form next in prominence, the second order tetragonal prism  $a = \{100\}$ , in order to get the outline of its front face we draw a line parallel to axis  $b$ , so as to cut off as much of  $r$  as the front  $a$ -face was observed to do on the crystal, and intersecting the two front equatorial edges of the bipyramid  $r$  at the two points P. Where the line cuts the axis  $a$ , at M, a line is drawn parallel to the axis  $c$ , as the plane  $a$  is also parallel to this axis as well as to axis  $b$ ; this vertical line cuts the front polar edges of  $r$  at the two points N. If we join the four points P and N by the four lines PN we obtain the directions of the edges between  $r$  and  $a$ , and the middle part of each line PN is actually the representation of the edge itself. But we have a further modifying form to draw in before we can determine how much this is in each case, namely the form  $e = \{101\}$ , the primary tetragonal bipyramid of the second order. In order to find the shape of the  $e$ -faces we proceed in a similar manner; for the upper front face we take a line P'P' parallel to the axis  $b$ , as  $(101)$  is parallel to that axis, cutting the equatorial edges of  $r$  at P' and P' and the axis  $a$  at M'. From M' a line M'N' is drawn parallel to a line joining A and C, as the plane  $(101)$  cuts off unit intercepts from the axes  $a$  and  $c$ . Then the two lines P'N' will be the directions of the edges between  $r$ - and  $e$ -faces, and the upper part terminating at N' will be the representation of the actual edges themselves. The two points where these lines cut the directions PN of the  $a$ -faces already determined fix the position of the horizontal edge of intersection between the  $a$  and  $e$ -face, which may be drawn in parallel to the axis  $b$ ; and they also determine how much of each of the lines P'N' is the edge of the little  $e$ -face. The lower  $e$ -face is obtained precisely similarly, and the two other  $e$ -faces, as well as the  $a$ -face, to the right of the figure, are also determined in like fashion. The edges between  $a$ - and  $r$ -faces are all parallel to the polar edges of  $r$  (the continuous lines), and our knowledge of this fact alone would have enabled us to construct them; but the above is the systematic method, and the fact referred to may be used to confirm the accuracy of the drawing.

The other subsidiary faces are very easily constructed, all being merely narrow strips replacing the equatorial edges of  $r$ . Those of the tetragonal prism of the first order,  $m = \{110\}$ , are the central ones and relatively the broadest, and their short end edges of intersection with the adjacent  $a$ -faces are parallel to the vertical axis. The somewhat narrower faces of the first order bipyramid  $s = \{221\}$  come next the  $m$ -faces, one above and one below in each case, and their end edges of intersection with the  $a$ -faces are parallel to the bipyramid constructed in thin dotted lines from the corresponding intercept-points A, B, and  $2c$ ; and the similarly narrow faces of the primary bipyramid of the first order  $p = \{111\}$  are the outermost of these strip-faces, next to the  $r$ -faces, and their short end-edges of intersection with the  $a$ -faces are parallel to the primary bipyramid constructed from the unit intercepts A, B, C in thin broken-and-dotted lines.

This completes the drawing of the front half of the crystal. The back half is also

shown in Fig. 174 of Chapter XIII., which, as already stated, was reproduced from the thickened outline of Fig. 347 now given, by the tracing method.

Proceeding now to the drawing of the **topaz** measured and discussed in Chapter XV., the construction is given in Fig. 348, for both the back and front halves, as the two are not quite the same, owing to the presence of two important forms,  $o=\{111\}$  and  $x=\{123\}$ , on the front half only, where each is represented by a single face. Hence the tracing method has only been employed for the transference, and repetition without construction lines, of the crystal outline including the back faces in Fig. 195 (page 231) of Chapter XV., for the purpose of assisting the comprehension of the description of the crystal there given. All the front faces are lettered in Fig. 195, corresponding to the letters assigned

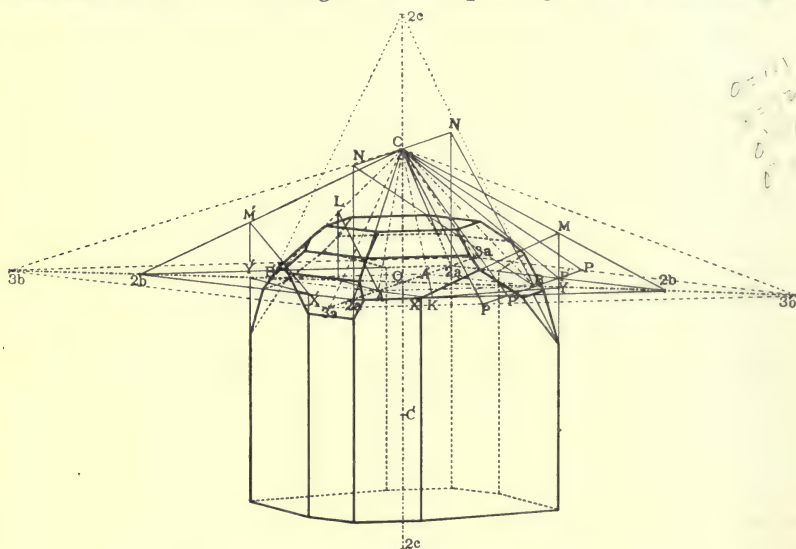


FIG. 348.—Construction of Crystal of Topaz.

to the various forms in the description, and frequent reference to it during the construction now to be described will be found very helpful, as the form letters are omitted in Fig. 348 in order not to confuse them with the construction letters.

The principal end form, which may be conveniently taken as the nucleus for the construction, is the rhombic pyramid  $o'=\{112\}$ , and this is drawn in Fig. 348, as it would appear if alone present, in thin continuous lines, joining the intercepts  $2a$ ,  $2b$ , and  $C$ . The parts of these lines which remain after the modifying forms have been drawn will actually represent edges on the crystal, as indicated by the thickening of those parts. The other well-developed pyramid above  $o'=\{112\}$  is  $o''=\{113\}$ , and the directions of its edges, supposing it alone present, are drawn in thin broken lines from the intercepts  $3a$ ,  $3b$ ,  $C$ ; the polar edges of this form, therefore, are drawn parallel to the corresponding broken lines terminating at  $C$ , representing the polar edges of the ideal pyramid, at such positions as to make this pyramid blunt the lower one  $o'$  to the extent observed on the crystal. The horizontal edges between the two pyramids are parallel to the equatorial edges of both pyramids, and indeed to



the primary rhombus formed by joining unit  $a$  and  $b$  intercepts, and which is the base of the primary pyramid  $o = \{111\}$  drawn in broken-and-dotted lines. The edges of the basal plane forming the flat upper termination of the crystal are also parallel to this same rhombus, and may at once be drawn in, at such positions as to give to the basal plane the relative size to which it was observed to be developed on the crystal. The back  $o'$  and  $o''$  faces had also better be drawn in thick dotted lines, as the tracing method cannot be employed so well here, owing to the absence of any primary  $o$ -face behind.

It is most convenient to draw next the prism faces, assuming for the moment the presence of only the pyramids  $o'$  and  $o''$ , as these alone are fully developed as regards the number of their faces. From  $2a$  downwards the edge between the two front  $p$ -faces (110) and (1 $\bar{1}$ 0) may be drawn parallel to axis  $c$ , as this would appear to be its approximate position on the crystal, the single  $o$ -face, however, to be subsequently drawn, replacing the solid angle at  $2a$ . We next draw one of the edges between a  $p$ -face, say the right-hand front one, and the  $p'$ -face (120) adjoining it on the extreme right, giving it the relative position seen on the crystal, that is, so as to leave the observed relative width of  $p$ -face. The same may be done for the left-front and the two back (to be dotted)  $pp'$  edges.  $X$  and  $X'$  are suitable points in front. We next determine the extreme right and left edges, those between the large  $p'$ -faces, there being no brachy-pinakoid present to blunt them. To find these edges, we draw from  $X$  and  $X'$  lines  $XY$  and  $X'Y'$  cutting the  $b$  axis at  $Y$  and  $Y'$ , parallel to the lines obtained by joining  $2a$  and  $B$ , the intercepts of  $p' = \{120\}$ . The required edges are then got by drawing lines downwards from  $Y$  and  $Y'$  parallel to the vertical axis.

The edge between  $p'$  and  $o'$  is obtained in each case by continuing these lines upwards to  $M$  and  $M'$ , where they cut the continuous lines representing the outer edges of the ideal pyramid  $o'$ ;  $XM$  and  $X'M'$  are then the directions of the required edges  $o'p'$ .

We can next find the directions of the edges of the faces  $q = (011)$  and  $q' = (021)$ . The edges between  $q$  and the basal plane above it, and between  $q$  and  $q'$  below it, are parallel to the axis  $a$ , the  $a$  index being 0 for all three forms. We may begin, therefore, by drawing the two basal-plane edges parallel to axis  $a$  and of such a size as represents what was observed on the crystal itself. The directions of the edges between  $o''$  and  $q$  are obtained by finding the intersection of the two planes in the usual manner, namely (the plane  $o''$  being already drawn in broken lines joining  $3a$ ,  $3b$ , and  $C$  its intercepts), by drawing a line through  $B$ , the  $b$ -intercept of  $q$ , parallel to axis  $a$ , and joining the two points  $P$ , where this line cuts the equatorial edges of  $o''$ , to  $C$ , the vertical intercept of both  $o''$  and  $q$ . The two lines  $CP$  are then the directions of the required  $qo''$  edges. Similarly  $CP'$  are the two directions of the edges between  $o'$  and  $q$ , for the two points  $P'$  are those where the line parallel to the axis  $a$  cuts the thin continuous lines representing the base of the pyramid  $o'$ . The directions of the remaining edges of  $q$ , those between it and the prism  $p' = \{120\}$ , are obtained by similarly drawing a line through  $C$  parallel to the axis  $a$ , and raising lines from  $2a$ , the intercept of  $p'$  on axis  $a$ , parallel to the vertical axis, and cutting the line through  $C$  at  $NN$ . Then  $NNB$  represents the section of the prism faces (120) and ( $\bar{1}$ 20) by the plane (011), assuming both to be completely developed, and the lines  $BN$  are consequently the directions of the front and back edges between  $p'$  and  $q$ , which are, therefore, drawn in parallel thereto.

To get the directions of the edges between  $q' = (021)$  and  $p' = (120)$  the simplest course is to draw a line from the centre of the edge between  $q'$  and  $q$  (which edge is parallel to the axis  $a$ ) parallel to the dotted line joining the intercepts of  $q'$ ,  $B$  and  $2c$ . Where this cuts the extreme right-hand edge of the prism, the edge  $p'p'$ , will be the apex of the isosceles-triangular face  $q'$ , and the edges required are obtained by joining this point to the ends of the edge between  $q$  and  $q'$ .

The  $q$  and  $q'$  faces on the left-hand side of the crystal are obtained similarly, but

in order not unduly to complicate the drawing some of the construction lines are omitted.

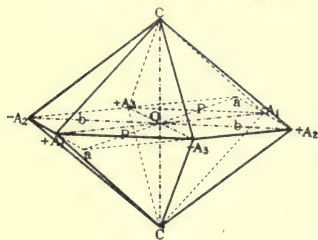
The only developed face of the primary pyramid  $o = \{111\}$ , a somewhat large one having the indices  $(1\bar{1}1)$ , and also the small single face of  $x = \{123\}$  in the same left front octant, are lastly to be inserted. The edge between  $o$  and the  $p$ -face  $(1\bar{1}0)$  below it, and also that made with the  $o'$ -face above it, are both parallel to the line joining unit intercepts on the  $a$  and  $b$  axes, and therefore to the edges between  $o'$  and  $o''$  and between  $o''$  and the basal plane; for  $c$ ,  $o''$ ,  $o'$ ,  $o$  and  $p$  all belong to the same zone. To find the direction of the edge between  $o = (1\bar{1}1)$  and  $p' = (1\bar{2}0)$ , we draw the two planes and find their intersection in the usual manner. The former is already drawn in broken-and-dotted lines; if we draw the latter, its intercepts on the  $a$  and  $b$  axes are  $2a$  and  $B'$ , but such a plane parallel to the vertical axis would only touch the former at the single point  $B'$ , and to bring about the intersection we move it parallel to itself until  $2a$  becomes  $A$ , when the intercept on the  $b$  axis is  $\frac{1}{2}b$ . Raising a vertical line here, as  $p'$  is parallel to the vertical axis, it cuts the outer polar edge (broken-and-dotted) of the pyramid  $o$  at  $L$ , and  $LA$  is therefore the direction of the required edge between  $o$  and  $p'$ , and the edge itself can at once be drawn in parallel to  $LA$ .

The edge between  $o$  and  $o'$  may readily be found by producing the basal edge of the former, as ideally indicated by the broken-and-dotted line  $AB'$ , so as to meet the right-hand basal edge of the latter, joining  $2a$  and  $2b$ , which it does at  $K$ , when  $CK$  is the direction of the required edge, which may be drawn parallel thereto. The fifth edge between  $o$  and the right-hand  $p$ -face is then to be inserted by joining up the first and fourth edges.

As regards the small  $x$ -face, much constructive trouble is saved by remembering that the face lies in the same zone with  $q$  and  $o'$ , so that its longer edges will be parallel to the edge  $qo'$  which they replace; also that its upper inclined edge will be parallel to the edge between the two front  $o'$ -faces, because it also lies in the same zone with those faces (see stereographic projection, Fig. 196, page 232). The fourth edge is thus automatically determined, as it merely joins the other ends of the longer edges, the relative distance apart of which will have been fixed by the direction of the upper inclined edge just referred to.

This completes the construction of the crystal of topaz, except as regards the lower cleavage plane termination, the edges of which are at once obtained by merely drawing them parallel to the lines joining the intercepts on the  $a$  and  $b$  axes proper to the two prisms, unit intercepts in the case of  $p$ , and  $2a$  and  $B$  or  $B'$  in the case of  $p'$ .

**Hexagonal Axes.**—In the case of the axes of a hexagonal crystal we have to draw the projection of three equal horizontal axes mutually





length, a value which is such as makes the rhombus formed by joining the ends the projection of one of  $120^\circ$  angle. Each half of the axis  $a$  (the front and the back half) is then bisected, and through the bisecting points  $P$  lines are drawn parallel to the axis  $b$  until they intersect the sides of the rhombus, which they also do at a projected angle of  $120^\circ$ . The projection of a hexagon is thus produced, the corners of which are the terminal points of the three horizontal axes, mutually inclined at  $120^\circ$ . When the vertical axis has also been given its proper length, in accordance with the axial ratio, we have a correct representation of the hexagonal axes, strictly comparable to the cubic, tetragonal and rhombic ones. By joining the ends of these hexagonal axes we at once produce the primary hexagonal bipyramid of the first order, the symbol of which is  $\{10\bar{1}1\}$ ; for each face meets the vertical axis and two of the horizontal axes at unit intercepts and is parallel to the third horizontal axis, as will be clear from Fig. 349.

The three horizontal axes are lettered  $A_1$ ,  $A_2$ , and  $A_3$  in Fig. 349, and the two halves of each are marked respectively positive and negative, according to the scheme described on the first page (299) of Chapter XX. concerning hexagonal crystals.

The most practical illustration will be to take the case of the construction of the crystal of **apatite** (Fig. 263, page 313), which was worked through in Chapter XXI. as the typical example of a hexagonal crystal, and this will next be proceeded with.

The length of the  $c$ -axis in Fig. 349 relative to the lengths of the horizontal axes, is that of apatite, namely 0.7345, and these axes are repeated in Fig. 350, in which the construction for apatite is given. They are produced to double their length, however, as intercepts of two unit lengths will frequently be required from the nature of the forms present. Fig. 263, page 313, was traced from the completed Fig. 350, leaving out the construction lines.

The method of procedure has now been so fully elucidated that a detailed description of this construction will not be necessary. It will suffice to say that the prism edges of  $m = \{10\bar{1}0\}$ , and  $n = \{11\bar{2}0\}$ , and of the only developed face of  $p = \{21\bar{3}0\}$ , are all parallel to the vertical axis; the horizontal edges of the first order prism  $m$  are parallel to the three horizontal axes in turn and are got by joining adjacent axis-ends, while those of the second order prism  $n$  are got by joining alternate axis-ends. The polar edges (those intersecting at the pyramid-apex) of the three pyramids are parallel to the directions obtained by joining the respective intercepts on axis  $c$  with the intercepts on the three horizontal axes, these directions being indicated in Fig. 350 by thin lines; the intercepts in the case of the most largely developed pyramid  $o' = \{20\bar{2}1\}$  are  $2c$  and unit intercepts on each of the two horizontal axes concerned, while for  $o = \{10\bar{1}1\}$  the less extensively developed primary pyramid the intercept on  $c$  is also of unit length. In the case of the small upper pyramid  $o'' = \{10\bar{1}2\}$  the  $c$ -intercept remains of unit length but the intercepts on the horizontal axes concerned are now of double unit length. All the horizontal edges are parallel to those between the lowest pyramid and the prism  $m$ , and these directions in the case of the top pyramid also define the contour of the terminal basal plane  $c$ . The long edges of  $q = \{11\bar{2}1\}$  are parallel to the polar edges of  $o'$ , which edges they replace, and the short inclined upper edges between  $q$  and  $o$  are parallel to the other polar edge of the same  $o$ -face in each case, as each  $q$ -face lies in the same zone with the pair of  $o$ -faces



on either hand. The only face requiring much consideration is the single face of the form  $s = \{21\bar{3}1\}$ , and even here the fact that this face lies in the two zones with the  $q$ - and  $o$ -faces above it to the right, and with the  $o'$ - and  $q$ -faces above it to the left respectively, at once gives the directions of the two edges meeting at the upper angle. We can readily find the direction of the edge between  $m$  and  $s$  by the usual method of finding the intersection of two planes. The intercepts of  $s$  are  $\frac{2}{3}A_1$ ,  $3A_2$ ,  $-A_3$ , and  $3c$ . The essential lines joining these intercepts are given in the figure, and if we raise a vertical line (parallel to axis  $c$ ) from  $A_1$  (on the line  $A_1 - A_3$  representing the plane  $m$ ), it cuts the plane  $s$  at  $P$ , and  $-A_3P$  is the direction of the required edge between  $m$  and  $s$ . The edge  $ns$  follows, the other three being known. The little

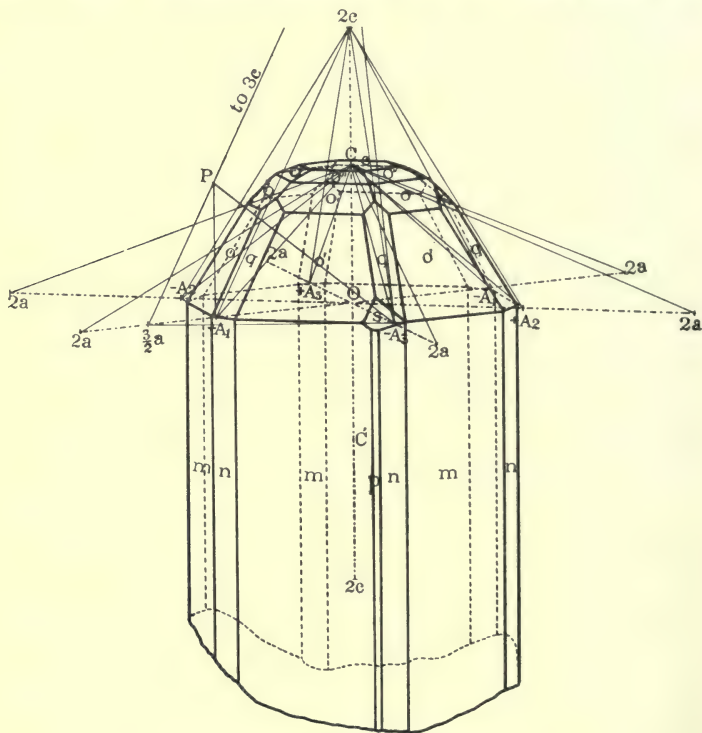


FIG. 350.—Construction of Crystal of Apatite.

edge between  $s$  and  $p$  is parallel to the line joining  $\frac{2}{3}A_1$  and  $-A_3$ , as both the pyramid  $s$  and the prism  $p$  have these intercepts in common, and lie in the zone  $[csp]$ . (See Fig. 264 for stereographic projection.)

**Trigonal Axes.**—The most convenient method of drawing trigonal crystals is to treat them as if they were hemihedral hexagonal crystals and to employ the hexagonal axes. At any rate, these can and must be employed to draw the primary pyramid or rhombohedron, the edges of which are the directions of the three trigonal axes. As the Bravais-Miller ratio of the hexagonal axes,  $a:c$ , is usually given as well as the Millerian rhombohedral axial angle, there is no difficulty about the use of the hexagonal axes, and the symbols of the forms present are

also generally given according to both notations. But if not, it is much easier to draw first the rhombohedral axes from the hexagonal ones, rather than to start directly to draw the rhombohedral axes.

The two practical examples worked out in Chapter XXIII., quartz and calcite, will be taken to illustrate the drawing of trigonal crystals. Quartz affords an illustration of trapezohedral hemi-hexagonal symmetry, and calcite a capital instance of rhombohedral hexagonal hemihedry,

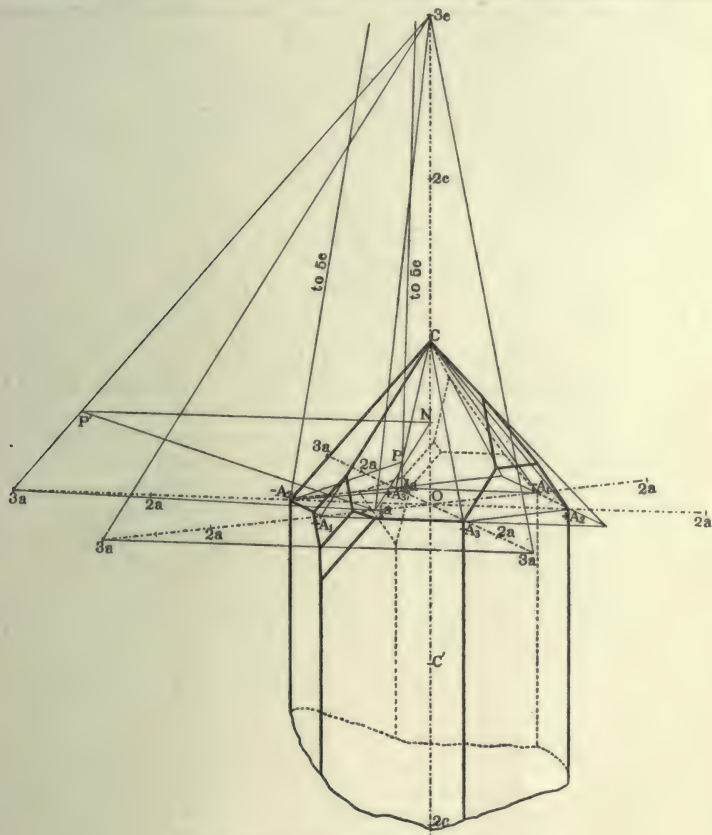


FIG. 351.—Construction of Crystal of Quartz.

and will afford us the opportunity of illustrating the construction of the rhombohedral Millerian axes.

**Quartz.**—The construction of the left-handed crystal described in Chapter XXIII. is shown in Fig. 351, and Fig. 321 (page 363) given to illustrate it in that chapter, and on which the letters indicating the various faces are marked, was reproduced by tracing the final form of the crystal, as shown by the thick lines, from Fig. 351.

The hexagonal axes were drawn as already indicated, giving the  $c$ -axis the relative length (1.1 of the cubic  $c$ ) indicated by the Bravais-Miller axial ratio. The

directions of the edges of the first order hexagonal prism  $m$  are obviously got by drawing lines parallel to the vertical axis through the six ends of the three horizontal axes. Those of the two complementary rhombohedra, the primary direct one  $r$  and its inverse form  $r'$ , behave just as an ordinary hexagonal pyramid of the first order for the purposes of drawing, but the individual faces are, of course, to be given the relative amounts of development actually shown on the crystal. The directions of the six polar edges are parallel to, or actually, those obtained by joining unit  $C$  with the ends of the horizontal axes. Four of the faces, all three  $r$ -faces and one  $r'$ -face, are about normally developed, but the other two  $r'$ -faces are relatively smaller. The edge between the right-hand  $m$ -face and the front  $r$ -face, which is developed owing to the smallness of the right  $r'$ -face, is parallel to the edge  $rr'$  between the front  $r$ -face and the left  $r'$ -face, as may be seen should be the case by a reference to the stereographic projection given in Fig. 322, for all these three faces  $m$ ,  $r$ , and  $r'$  belong to the same zone. Similarly, the edge between the same  $m$ -face and the right-back  $r$ -face is parallel to the edge between that right-back  $r$ -face and the smaller back-central  $r'$ -face.

The only faces requiring any considerable thought are those of  $s$ , the left trigonal pyramid of the second order  $\{4\bar{2}1\} = \{2\bar{1}\bar{1}1\}$ , and of the adjacent form  $x$ , the left positive trapezohedron  $\{4\bar{2}1\} = \{6\bar{1}\bar{5}1\}$ . It will be clear from the projection (Fig. 322), however, that the edge  $sx$  is parallel to the opposite outer edges  $r's$  and  $mx$ , and that these three parallel edges are also parallel to the edge  $r'r$ , between the  $r'$ -face next to  $s$  and the back-left  $r$ -face beyond it. For the front  $m$ ,  $x$ ,  $s$ ,  $r'$ , and left-back  $r$ -faces all belong to the same zone; moreover, the zone is continued by the small elongated back  $s$ -face and the middle back  $m$ -face, so that the two dotted longer  $s$ -edges are also parallel to this same direction. Next, the other two front  $s$ -edges,  $ms$  and  $sr$ , are parallel to the edge  $rr'$  between the front  $r$ -face and the right-front  $r'$ -face, for the faces concerned all belong to the same zone. The same kind of consideration applies to the two other faces of the little elongated back  $s$ -face, for these two shorter edges are parallel to the edge  $r'r$  between the middle-back  $r'$ -face and the right-back  $r$ -face, already alluded to as being parallel to the extreme right  $mr$ -edge. Also the left-back (dotted)  $xm$  edge is parallel to the same direction. Thus all the  $s$ -edges and a pair of edges of each  $x$ -face are entirely determined by making use of the zonal relationships, without any intersections.

The only edges requiring intersections to be constructed are the two remaining edges of each of the pair of  $x$ -faces, and either of the two in each case will suffice, the other being determined automatically. The Bravais-Miller indices of the front  $x$ -face are  $(6\bar{1}\bar{5}1)$ , and the intercepts may most conveniently be written  $A_1$ ,  $-6A_2$ ,  $-\frac{2}{3}A_3$ ,  $6C$  (that is,  $5A_1$ ,  $-30A_2$ ,  $-6A_3$ ,  $30C$  all divided by 5), and as we only need  $A_1$ ,  $-A_2$ , and  $C$  in drawing the plane we can halve the values along these three axes in order to get the drawing into reasonable compass and thus actually use  $\frac{1}{2}A_1$ ,  $-3A_2$ ,  $3C$ . These three intercepts are joined in Fig. 351 with thin lines to represent the plane  $x$ . To find now its intersection with the front  $r$ -face in order to determine the direction of the edge  $rx$ , we need only push the  $r$ -plane back until its intercept on  $A_1$  is also  $\frac{1}{2}a$ , when it will cut  $C$  at  $\frac{1}{2}c$  marked by the letter  $N$ ; and as  $r$  is parallel to the axis  $A_2$  a line  $NP'$  may be drawn parallel to that axis. The points  $P'$  and  $\frac{1}{2}a$  will thus be common to the two planes, and the line joining them will consequently be the direction of their intersection, and the edge  $rx$  should be drawn parallel thereto, from the corner of the  $s$ -face already drawn. The fourth edge bounding  $x$ , namely  $mx$  (left  $m$ ), may also be at once drawn in, for the third edge  $mx$  being known to be parallel to  $sx$  can be drawn so, and the ends of the fourth are thereby fixed. The back  $x$ -face is to be completed in the same way. The indices of this face are  $(\bar{1}\bar{5}\bar{6}1)$ , and the most convenient mode of writing the intercepts is  $-5A_1$ ,  $-A_2$ ,  $\frac{2}{3}A_3$ ,  $5C$ . Joining  $-A_2$ ,  $\frac{2}{3}A_3$ , and  $5C$  to represent the plane  $x$ , and also remembering that the back-left  $r$ -face is represented by the lines joining  $-A_2$ ,  $+A_3$ , and  $C$ , it will be obvious that the point  $-A_2$  is common to the two planes, and that  $P$  is a point of inter-



section; the line joining these two points is, therefore, the required direction of the edge  $rx$ . The fourth edge of this back  $x$ -face is determined automatically, for three edges are now known, and the ends of the fourth are thereby fixed.

**Calcite.**—The crystal of calcite described in Chapter XXIII., and illustrated in Fig. 326, page 372, is primarily a combination of the same first order hexagonal prism  $m$  as in the case of quartz with the direct primary rhombohedron  $r = \{100\} = \{10\bar{1}1\}$  and the inverse obtuse rhombohedron  $e = \{110\} = \{01\bar{1}2\}$ . Before proceeding to the actual construction of the measured crystal, it will be useful to draw separately these two rhombohedra, which are not the complementary direct and inverse pair, together making up a hexagonal pyramid as in the case of quartz, but the direct and inverse representatives of quite distinct rhombohedra, which under the older method of regarding crystal structure would be considered as the opposite hemihedral halves of two different hexagonal pyramids. Moreover, the construction of the primary rhombohedron  $r = \{10\bar{1}1\}$  gives us the construction of the rhombohedral Millerian trigonal axes.

The construction of this primary rhombohedron is shown in Fig. 352, and that of the obtuse inverse rhombohedron  $e = \{01\bar{1}2\}$  in Fig. 353. In calcite the two rhombohedra are often formed on the same crystal, the obtuser one (Fig. 353) blunting the upper termination of the primary one.

In the case of the primary rhombohedron  $r = \{10\bar{1}1\}$  the directions of the three upper and three lower polar edges, terminating respectively at the apices  $C$  and  $C'$ , are found by drawing the triangular bases of the two alternating (upper and lower) trigonal pyramids and joining their corners to the points  $C$  and  $C'$ , which are such that  $OC$  and  $OC'$  have the length corresponding to the value of  $C$  in the axial ratio  $a : c$ . Drawing, therefore, first the hexagonal axes and giving  $OC$  and  $OC'$  the length

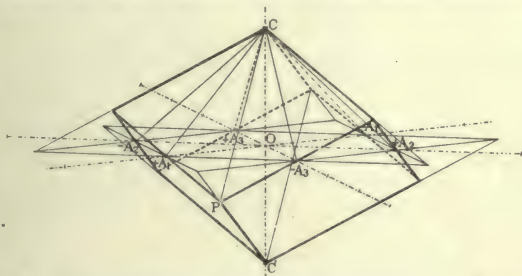


FIG. 352.—Construction of Primary Rhombohedron  $r = \{100\}$ .

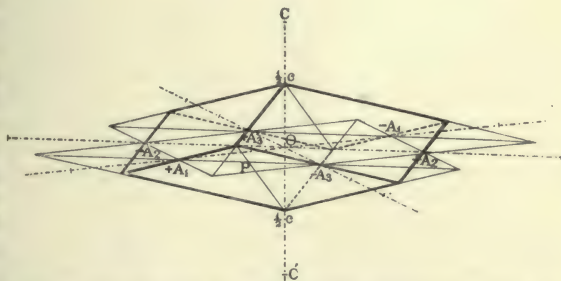


FIG. 353.—Construction of Inverse Obtuse Rhombohedron  $e = \{110\}$ .

0.8545 of the usual length for a cubic crystal, corresponding to the axial ratio of calcite, we proceed to find the two bases in question. The upper front  $r$ -face is a lateral expansion of  $+A_1$ ,  $-A_3$ ,  $C$ , and so we produce the line  $+A_1$ ,  $-A_3$  indefinitely on each side. We similarly produce  $-A_1$ ,  $+A_2$ , and  $-A_2$ ,  $+A_3$  corresponding to the two other (back) upper faces of the trigonal pyramid, and from the corners of the basal triangle produced by the intersection of these three lines we

draw lines to, and meeting in, C, the apex of the upper pyramid. We then next construct the base of the lower pyramid by similarly producing the other three edges of the basal axial hexagon until they meet, and from its three corners draw lines to C', the apex of the lower alternate pyramid. We have now only to find how these two trigonal hemi-pyramids intersect. We know that opposite faces are parallel, and also that all the edges of the rhombohedron fall into three sets of four each, those of each set being parallel to one of the three polar edges. We have already determined two of the four in each set, for each lower polar edge is parallel to the opposite upper one. One point of intersection will, therefore, give us all we require, the direction of the edge starting from this point being known. The simplest intersection to find is that of the lower middle polar edge C'P with the upper front *r*-face. This can be found by drawing a central line down the face, from C to the centre of the line joining  $+A_1$  and  $-A_3$ , and producing it till it cuts the lower middle polar edge in question at P. From P we can then at once draw lines parallel to the right and left upper polar edges, and thus complete the upper front face of the rhombohedron. From the right and left corners of this face we can then also draw lines parallel to PC' and thus complete the two front lower faces. The right and left corners of these in turn determine the two remaining long back dotted edges, after drawing which the figure of the rhombohedron is complete.

The three directions of the polar edges are those of the Millerian axes. When it is desired to employ these axes in the further drawing of any trigonal crystal, it is only necessary first to draw them parallel to the directions of these three rhombohedral edges and so as to pass through and intersect at the centre O, as is done in Fig. 274 (page 330), the rhombohedron in which has been traced from this in Fig. 352.

The obtuse inverse rhombohedron  $e = \{01\bar{1}2\}$  was constructed in Fig. 353 in a precisely similar manner to the primary rhombohedron. The intercepts on the two horizontal axes are now, however, double of the unit value, while the intercept on the vertical axis remains of unit length. It is most convenient to take half OC as the vertical intercept and thus to retain the unit lengths of the horizontal axes. The same basal triangles are then employed as for the primary rhombohedron, but their corners are joined to  $\frac{1}{2}c$ , instead of to C; and as the rhombohedron is an inverse one instead of a direct one, the basal triangle which was connected to C is now connected to  $\frac{1}{2}c$  below, and that which was connected to C' is now connected to  $\frac{1}{2}c$  above.

In the cases of both rhombohedra it will be observed that the ends of the horizontal hexagonal axes bisect respectively the six edges other than the polar ones.

We may proceed now to the drawing of the crystal of calcite (Fig. 354). The long edges of the prism *m*-faces may be constructed by drawing lines through the ends of the horizontal axes parallel to the vertical axis. The primary rhombohedron *r* may also be drawn just as in Fig. 352. The three upper faces of the obtuse rhombohedron *e* are then to be drawn, so as to blunt and replace the upper apex of the primary rhombohedron. The longer edges of this form, and also of the two faces developed of the scalenohedron  $t = \{310\} = \{21\bar{1}3\}$  (for lettering of faces see Fig. 326, which was traced from the finished outline of Fig. 354), are parallel to the polar edges of *r*, as may be seen from a consideration of the stereographic projection in Fig. 327, for the *t* and *e* poles lie in the same zone in each case as a pair of *r* poles, and between the latter. The only part of Fig. 353 which appears in the final outline of the calcite crystal is the portion of the polar edges about the apex. Having first drawn in this apex the longer *er*-edges may at once be drawn parallel to the original *r*-edges, giving the *e*-faces the approximate relative size actually observed on the crystal, ignoring for the time being the modifying *t*-faces. The edges of the *m*-faces may next be conveniently completed, as far as they are determined by the *r*- and *e*-faces, ignoring preliminarily the faces of the third rhombohedron *n* and of the scalenohedron *v*. The front edge between the front *m*- and *r*-faces is the line joining  $+A_1$  and  $-A_3$ ; that between the left-back *m*- and *r*-faces is the line, now to be dotted,  $-A_2$ ,  $+A_3$ ; and that between

the right-back  $m$ - and  $r$ -faces, also to be dotted, is obtained by joining  $-A_1$  and  $+A_2$ . Both these dotted edges will remain unmodified, but the front edge  $mr$  is subsequently to be replaced by a narrow face, the only one developed on the crystal, of the rhombohedron  $n = \{3\bar{1}\bar{1}\} = \{40\bar{1}1\}$ , as well as by two little corner faces of the common scalenohedron of calcite,  $v = \{20\bar{1}\} = \{21\bar{3}1\}$ . The edges between the  $r$ -faces and the two  $m$ -faces on either side of the middle one in front, and between the middle back  $m$ -face and the  $r$ -faces, are parallel in each case to one of the polar edges of the ideal

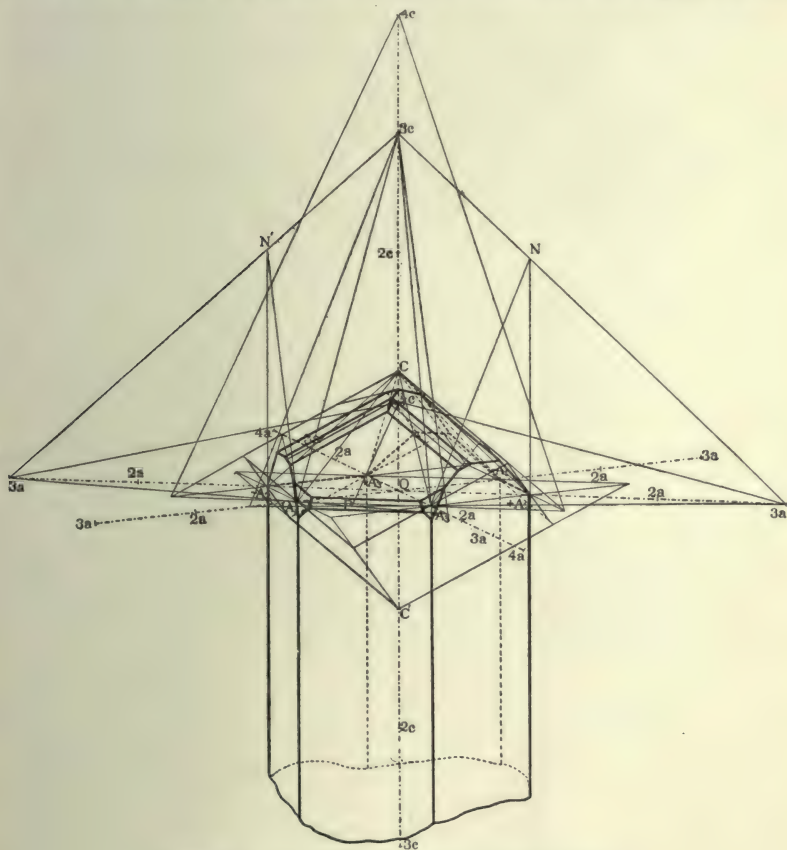


FIG. 354.—Construction of Measured Calcite Crystal.

hexagonal pyramid of which  $r$  is half, and the proper one is readily determined by a reference to the stereographic projection, or better still to that of quartz given in Fig. 322, as this latter gives the poles of all six pyramid faces ( $r$  and  $r'$ ). In our drawing of calcite all six theoretical edges are drawn in lightly, for use in drawing the  $mr$  edges parallel. The edges  $me$  are parallel to those three edges of the basal hexagon which are alternate to those which form the  $mr$  edges.

It now only remains to insert the smaller modifying faces of  $t$ ,  $n$ , and  $v$ . The little polar edge  $tt$  determines the two  $t$ -faces, as we know that the longer edges are parallel to the edges  $re$ . This polar edge is readily obtained by constructing the two  $t$ -planes and finding their intersection. The indices of the right-hand  $t$ -face are  $(21\bar{3}4)$ , and the



corresponding intercepts are  $6a$ ,  $12a$ ,  $4a$ ,  $3c$ , and as the three latter only are needed they may most conveniently be divided by 4 and written  $3a(\text{on} + A_2)$ ,  $a(\text{on} - A_3)$ , and  $\frac{3}{4}c$ . These intercepts are joined by thin lines in the drawing, and a similar set are drawn on the left side to represent the plane of the left-hand  $t$ -face. If the two bases of these triangles are produced inwards they meet at  $P$ , and the line joining  $P$  and  $\frac{3}{4}c$  is the required line of intersection of the two  $t$ -planes, and the little edge  $tt$  is to be drawn parallel thereto.

As regards the single  $n$ -face, it replaces the front horizontal edge  $mr$ , and its two long edges are parallel thereto. This face  $n$  belongs to an acute direct rhombohedron having the indices  $\{40\bar{4}1\}$ , and it is well known that its edges are directly replaced by the common scalenohedron of calcite  $v = \{21\bar{3}1\}$ . Hence the little edges  $nv$  will be parallel to the ideal edges of  $n$ . These are drawn in thin lines, the apex being at  $4c$ , the intercept on the vertical axis being 4 times the unit length, while the same unit base as was used for  $r$  is still valid for  $n$ . Hence the required directions of the edges  $nv$  are parallel to the lines drawn from  $4c$  to the right and left corners of the basal triangle. The edges between the  $v$ -scalenohedron faces (on the right and left front corners of the crystal) and the front  $r$ -face are parallel to the edges  $rt$ , and after having inserted them it only remains to find the directions of the edges  $vm$ . The indices of the right  $v$ -face being  $(21\bar{3}1)$ , its intercepts are  $3a$ ,  $6a$ ,  $2a$ ,  $6c$ , and as the last three suffice to determine the plane we may write them as  $3a(\text{axis} + A_2)$ ,  $a(\text{axis} - A_3)$ ,  $3c$ . This plane is constructed by joining these intercepts, in thin lines in the drawing. The right  $m$ -face is represented by the line joining  $-A_3$  and  $+A_2$ , and thus the two planes have the point  $-A_3$  in common. If we raise a line from  $+A_2$  parallel to the vertical axis  $N$  will be another point in common, for the line  $3c \cdot N$  lies in the vertical plane. Hence a line joining  $-A_3$  with  $N$  is the required intersection, and the little edge  $vm$  must be drawn parallel to it. Treating the left-hand planes  $v$  and  $m$  in the same manner, the line joining  $+A_1$  with  $N'$  is the direction of this left intersection  $vm$ , and the edge between the left-front  $m$ -face and the left  $v$ -face should be drawn parallel to it.

The fourth edge of each  $v$ -face, the edge between it and the front  $m$ -face, is then at once automatically determined, the other three edges having been drawn. But its direction in each case may be readily verified, for the two directions are parallel respectively to the edges of the primary pyramid  $+A_2C$  and  $-A_2C$ .

This completes the drawing of the crystal of calcite.

**Monoclinic Axes.**—We now revert to the system of three axes, but while one remains perpendicular to the plane of the other two, those two latter may be arranged at any angle other than  $90^\circ$  in that plane. One of these two is chosen as the vertical one, and labelled  $c$  as usual; so monoclinic symmetry simply amounts to the other axis being inclined to the vertical axis at an angle which is not a right angle, while remaining at right angles to the first axis. This first axis, known as the symmetry axis, perpendicular to the axial plane  $ac$ , is lettered  $b$ , and remains of the unit length of the cubic axes. The vertical axis  $c$  requires to be given the length corresponding to  $c$  in the axial ratio  $a:b:c$ , which is really  $a:1:c$ , as  $b$  is retained as unity according to the usual convention. The only new problem, therefore, is to find the direction of the inclined axis  $a$ , and then to give it its proper length as indicated by the axial ratio.

In Fig. 355 the cubic axes are represented as usual by  $AA'$ ,  $BB'$ , and  $CC'$ . From the centre  $O$  we mark off a length  $OP$  along  $OC$ , such that

$$OP = OC \cdot \cos \beta$$

where  $\beta$  is the acute angle between the inclined axes (the supplement of the obtuse axial angle usually given in descriptions of monoclinic crystals). The author's method of carrying this out in practice is to express OC in millimetres, reading to a tenth of a millimetre with the aid of a good scale, and to add the logarithm of this to that of  $\cos \beta$ , the sum being the logarithm of OP also expressed in millimetres and decimals of such, which can then be marked off along OC with the aid of the scale.

Next, from the centre O a length OQ is marked off from OA' in a similar manner, such that

$$OQ = OA' \cdot \sin \beta.$$

Lines are then drawn from P and Q respectively parallel to OA' and OC. Their point of intersection, A'', is a point on the inclined  $a$ -axis; A'' is joined to O, therefore, and the line produced for an equal distance to A''. A''A''' is then the direction of the inclined axis, and would represent it at its proper length also if the relative length to the unit axis  $b$  were also unity. As this is not so, however, the proper length must be given to it, by multiplying its actual length in the drawing by the value of  $a$  in the axial ratio  $a:b$ . The vertical axis must also be given its proper length corresponding to the ratio  $c:b$ , by multiplying OC by the value of  $c$ ; or if the cubic-axial templet be used, the value of  $c$  is marked off from the scale on the templet edge, both above and below the centre. In Fig. 355 the lengths of the  $a$ - and  $c$ -axes,  $aa'$  and  $cc'$ , are those for ammonium magnesium sulphate, a crystal of which salt was described and worked through practically in Chapter XVII. In this case the axial ratio is:  $a:b:c = 0.7400:1:0.4918$ , and the axial angle  $\beta = 107^\circ 6'$ .

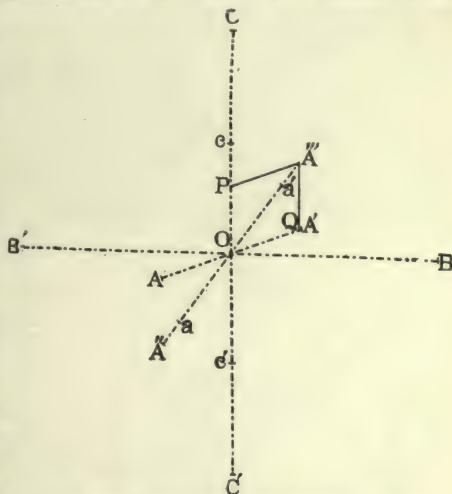


FIG. 355.—Construction of Monoclinic Axes.

The actual calculations for OP and OQ are as follows:

In the original drawing, of which Fig. 355 is a half-size reproduction,

$$OA' = 15 \text{ millimetres and } OC = 44.5 \text{ mm. Acute } \beta = 72^\circ 54'.$$

$$\text{Log. OC} \quad 1.64836$$

$$\text{Log. OA'} \quad 1.17609$$

$$\text{Log. } \cos \beta \quad 1.46841$$

$$\text{Log. } \sin \beta \quad 1.98036$$

$$\text{Log. OP} \quad 1.11677 \quad \text{OP} = 13.1 \text{ mm.} \quad \text{Log. OQ} \quad 1.15645 \quad \text{OQ} = 14.3 \text{ mm.}$$

The drawing of this crystal will next be considered, employing the axes just drawn, as an illustration of the construction for a monoclinic crystal.

**Ammonium Magnesium Sulphate.**—The construction for Fig. 215, page 258, the illustration in Chapter XVII. representing the crystal measured, is given in Fig. 356. It is quite similar to that for a rhombic crystal, except that the basal plane  $c$  is now tilted downwards towards the observer, parallel to the inclined axis  $a$ , instead of forming a rectangular termination.

The edges  $cq$  and  $bq$  (see Fig. 215 for lettering of faces) are therefore parallel to the inclined axis  $a$ , which is their zone axis. The edges of the prism zone,  $pp$ ,  $pp''$ ,  $p'''b$

are parallel to the vertical axis  $c$ , which is similarly their zone axis, as in the case of a rhombic crystal. The edges  $cr'$  are similarly parallel to the symmetry axis  $b$ . Moreover, the  $co$ ,  $op$ ,  $po'$  and  $o'c$  edges are all parallel to the line AB joining unit intercepts along the  $a$  and  $b$  axes, for  $c$ ,  $o$ ,  $p$ , and  $o'$  are all primary forms belonging to the same zone. This will be rendered clear by a reference to the stereographic projection, Fig. 216, page 258.

Similarly, the edges  $oo$  and  $no$  are all parallel to the line AC joining unit intercepts along  $a$  and  $c$ ; for the pyramids  $o$  and  $n$  belong to a common zone which also includes the clino-pinakoid  $b$ . For a like reason the edge  $oq$  is parallel to BC.

These principal edges are thus all determined as regards their directions by their parallelism either to the axes themselves or to the edges of the primary pyramid produced by joining unit intercepts along them. The remaining edges can all be found by simple constructions for the intersection of the two planes meeting in each particular edge. The positions of the primary edges in Figs. 356 and 215 are such as

fairly represent the relative development of the various faces actually exhibited by the crystal.

As regards the direction of the edges  $qn$  and  $np$ , the stereographic projection at once informs us that they are parallel to each other, and that they simply replace the edge  $qp$  without change of direction, for the  $q$ ,  $n$ , and  $p$  faces belong to the same zone. We could, therefore, simply find the intersection of  $q$  and  $p$ , but it is really quite as simple to find that of  $q$  and  $n$ , and possibly more instructive. The indices of  $n$  are (121) and the intercepts consequently  $2a : b : 2c$  or  $a : \frac{1}{2}b : c$ . These latter intercepts are joined by thin lines in Fig. 356, to represent the plane  $n$ . The plane  $q = (011)$  is represented by the line joining  $\frac{1}{2}b$ , and  $\frac{1}{2}c$ , for this is parallel to the unit intercept line BC, and by the line through  $\frac{1}{2}c$

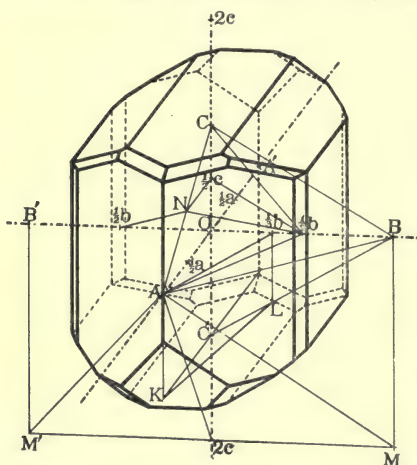


FIG. 356.—Construction of Measured Crystal of Ammonium Magnesium Sulphate.

parallel to axis  $a$ . The two planes thus drawn have common points at  $\frac{1}{2}b$  and N; hence, the line joining N and  $\frac{1}{2}b$  is the direction of the intersection and therefore of the required edge, which may be drawn parallel to it.

To find the direction of the edges  $pr'$  and the opposite  $r'o'$ , which are parallel to each other because they belong to the same zone, we draw lines through A and B parallel to the vertical axis  $c$  to represent the plane  $p = (110)$ ; to represent  $r' = (20\bar{1})$  we join A and the lower  $2c$ , as the intercepts of the latter on axes  $a$  and  $c$  are 1 and  $-2$  respectively, and through  $2c$  draw  $MM'$  parallel to the symmetry axis  $b$ , as  $r'$  is parallel to that axis. Then AM is the required intersection of  $p = (110)$  and  $r' = (20\bar{1})$ , while  $AM'$  is the intersection of  $p = (1\bar{1}0)$  with the same  $r'$  face,  $M'$  being at the intersection of the line parallel to axis  $b$  with a vertical line dropped from  $B'$ .

Finally, we have to find the intersection of  $p'''$  and the lower  $q$ . The indices of the former are (130) and the intercepts on axes  $a$  and  $b$  consequently 3 and 1 respectively, or more conveniently 1 and  $1/3$ . We join, therefore, A and  $1/3b$  to represent the plane  $p'''$ , also dropping a line from each of these intercepts parallel to the vertical axis  $c$ . To represent  $q = (01\bar{1})$ , the  $q$ -face in question, we join B and  $C'$ , and through  $C'$  draw a line  $KC'$  parallel to the axis  $a$ , as the  $q$ -faces are parallel to this axis. Then KL, joining the points of intersection K and L with the two vertical lines from A and  $1/3b$ , is the direction of the edge  $qp'''$  required. A similar construction for the com-



plementary edge on the other side of the figure completes the construction, for the few small remaining edges are determined automatically, it being only necessary to join up the ends of those now constructed, in the few places where gaps have been left.

**Triclinic Axes.**—Here we have lastly the most general case, where all three axes are mutually inclined at angles other than  $90^\circ$ . The angle between the axes  $b$  and  $c$  is  $\alpha$ , that between  $a$  and  $c$  is  $\beta$ , and that between  $a$  and  $b$  is  $\gamma$ . The construction is similar in principle to that for monoclinic axes, only carried out for two of the three instead of for one, the third axis remaining vertical; that is, the system of axes is arranged so that one of them is vertical, when it becomes only necessary to find the inclination of the other two to it and to each other.

We start, as always, with the cubic axes, drawn from the templet. They are  $AOA'$ ,  $BOB'$ ,  $COC'$  in Figs. 357 and 358, which represent the construction of the axes of two typical triclinic crystals, those

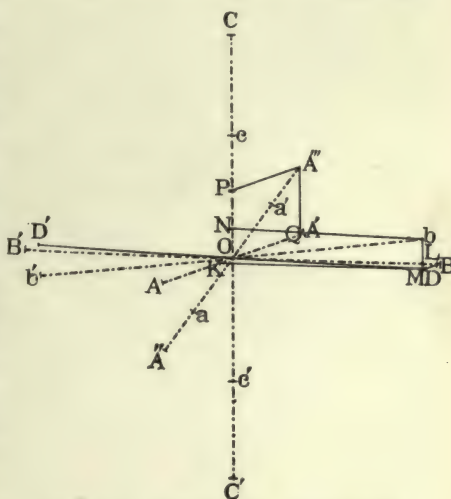


FIG. 357.—Construction of Triclinic Axes of Copper Sulphate.

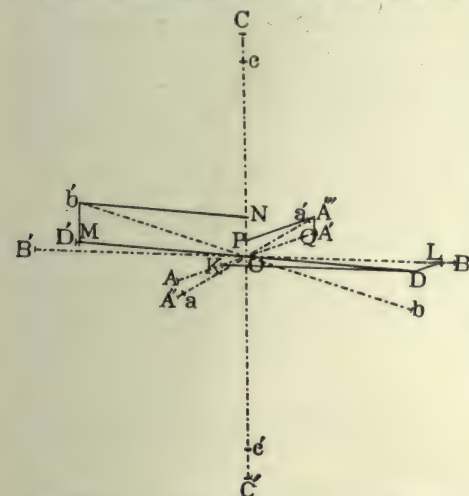


FIG. 358.—Construction of Triclinic Axes of Methyl Triphenylpyrrolone.

parallelogram is also drawn and produced to an equal length beyond O, that is to  $D'$ .

This diagonal, and the vertical axis  $c$ , form the projection of the pinakoidal plane

of copper sulphate and of methyl triphenylpyrrolone. Their half-lengths  $OA$ ,  $OB$ , and  $OC$  are most conveniently expressed in millimetres and decimals of such, for the purposes of the following simple calculations, as in the case of the calculation for the inclined axis of the monoclinic system.

Along  $OA$  we take the length  $OK$  such that

$$OK = OA \cdot \cos C,$$

where  $C$  is the angle between the pinakoidal faces  $(100)$  and  $(0\bar{1}0)$ ; and along  $OB$  we take the length  $OL$ , such that

$$OL = OB \cdot \sin C.$$

The lines  $KD$  and  $LD$  are then drawn parallel to the cubic axes  $b$  and  $a$  respectively, intersecting at  $D$ , and the diagonal  $DO$  of the

(100), and the diagonal OD itself is the projection of a line of unit length in that plane. We next use this diagonal as a base from which to construct the real triclinic axis  $b$ , by taking account further of the inclination  $\alpha$  of the axes  $b$  and  $c$  (which are parallel to the edges of intersection of the pinakoid {100} in question with the other two pinakoids {010} and {001}), that is, of the inclination to the vertical direction of that edge of the pinakoid (100) which is formed by its intersection with the basal pinakoid (001). To effect this we take a length OM along either OD or OD', according as the acute angle  $\alpha$  between the axes  $b$  and  $c$  is to the right or to the left (referring to the 2 upper quadrants), and such that

$$OM = OD \cdot \sin \alpha;$$

and along the vertical axis the length ON, such that

$$ON = OC \cdot \cos \alpha,$$

where  $\alpha$  represents the acute angle between the axes  $b$  and  $c$ .

We could equally well let  $\alpha$  represent the conventional angle, even though it be obtuse; but in this latter case, while OM would be unaffected, and would always be measured along OD', because  $\sin(180^\circ - \alpha) = \sin \alpha$ , ON would have to be measured downwards, on the lower or negative part of the vertical axis, for  $\cos(180^\circ - \alpha) = -\cos \alpha$ , and we are obliged to use the acute supplement in logarithmic calculation. This only produces the same geometrical result as before, however, for we simply construct Ob' (Fig. 357) instead of Ob. It is simpler on the whole always to take the acute  $\alpha$  and to measure the resulting OM along OD or OD' in the two several cases.

We then have the sides of another parallelogram the diagonal of which is the axis  $b$ , by drawing the lines Nb and Mb parallel to OD and the vertical axis. The point of their intersection is the termination of the axis  $b$ , and this gives its real length also, as the  $b$ -axis is taken as unity even in the triclinic system.

Having thus constructed the vertical axis  $c$  and the right-and-left axis  $b$ , it only remains to construct the front-and-back axis  $a$  by the method used in the case of a monoclinic crystal, for the plane (010) alone need now be considered, its edges being parallel to the vertical axis and to the axis  $a$  in question. The crystal is so disposed that the position of this brachy-pinakoid  $b = \{010\}$  in space is relatively the same as in the monoclinic and rhombic systems, as will be obvious from the fact that the two  $b$ -poles are also shown in the stereographic projection at the extremities of the horizontal diameters (Figs. 48, Chapter VI., and 228 in Chapter XIX.).

We take, therefore, OP along OC and OQ along OA', such that

$$OP = OC \cdot \cos \beta,$$

and

$$OQ = OA' \cdot \sin \beta,$$

where  $\beta$  is the acute angle between the axes  $a$  and  $c$ . Through P and Q the lines PA''' and QA''' are to be drawn parallel to the cubic axis AA' and to the vertical axis respectively. Then the diagonal A'''O is to be drawn and produced equally on the other side of O to A''. The line A''A''' is then the projection of the axis  $a$ , of unit length, however, as if it were equal to  $b$ .

It only now remains to give to the axis  $a$  thus constructed, and to the vertical axis  $c$ , their true lengths corresponding to the axial ratio,  $a : 1 : c$ , for the particular crystal-line substance under consideration.

In Fig. 357 the axes drawn are those for the typical triclinic substance described and practically worked through in Chapter XIX., copper sulphate, the axial ratio for which is :

$$a : b : c = 0.5715 : 1 : 0.5575.$$

The axial angles are :

$$\alpha = 82^{\circ} 16', \beta = 107^{\circ} 26', \gamma = 102^{\circ} 40'.$$

The value of  $\alpha$  being less than  $90^{\circ}$ , the upper acute angle between the axes  $b$  and  $c$  is thus to the right (compare Fig. 39, page 71, Chapter V.), and consequently OM is taken along OD and not along OD', which latter is perhaps more commonly the case with triclinic crystals.

In order to make this commoner case equally plain, Fig. 358 is added, representing the construction of the axes of methyl triphenylpyrrolone, a substance goniometrically investigated by the author, and the crystals of which form a particularly perfect example of triclinic symmetry, all the primary forms being developed, and at quite typical angles, although the substance was not suitable for the practical work recommended in Chapter XIX. on account of the difficulty and expense attending its preparation. A typical crystal of the substance is represented in Fig. 47 (page 98) and its stereographic projection in Fig. 48. Its axial ratio is :

$$a : b : c = 0.9059 : 1 : 0.8695,$$

and its axial angles are :

$$\alpha = 100^{\circ} 8', \beta = 93^{\circ} 57', \gamma = 109^{\circ} 34'.$$

It must be remembered that the angles conventionally quoted as the axial angles, and which, as here, are all three more commonly obtuse, are the following:  $\alpha$  is the upper-right angle between the axes  $b$  and  $c$ ,  $\beta$  is the upper-front angle between the axes  $a$  and  $c$ , and  $\gamma$  is the right-front angle between the axes  $a$  and  $b$ . This will be clear from Fig. 39, Chapter V. Sometimes the acute angles, the supplements of these, are given, but in such a case a statement ought to be made definitely specifying the angles referred to. Occasionally, as in the literature concerning copper sulphate, hopeless confusion has arisen owing to one or two out of the three axial angles having been given correctly, but the others or other having been expressed by their supplements, without any explanatory statement, and a full practical reinvestigation has alone been able to put the case straight. Hence, one cannot insist too strongly on the necessity for either following the convention, or for definitely specifying to which particular angles  $\alpha$ ,  $\beta$ , and  $\gamma$  refer; in fact it is safest to do both.

In the case of methyl triphenylpyrrolone, the value of  $\alpha$  being greater than  $90^{\circ}$  the supplementary upper acute angle lies to the left, and so OM is measured along OD', and not along OD as was the case with copper sulphate.

The actual calculations in the two cases were as follows :

The cubic axes in the original drawings, from which Figs. 357 and 358 are reproduced half-size, were of the lengths :

$$OA = 15 \text{ millimetres, } OB = 42 \text{ mm., and } OC = 44.5 \text{ mm.}$$



For Methyl Triphenylpyrrolone.

$C = \text{Angle } (100) : (0\bar{1}0) = 69^\circ 19'$

Acute  $\alpha = 79^\circ 52'$

Acute  $\beta = 86^\circ 3'$

Log. OA 1.17609

Log. cos C 1.54802

Log. OK 0.72411 OK = 5.3 mm.

Log. OB 1.62325

Log. sin C 1.97107

Log. OL 1.59432 OL = 39.3 mm.

OD' = 34.1 mm.

Log. OD' 1.53275

Log. sin  $\alpha$  1.99317

Log. OM 1.52592 OM = 33.6 mm.

Log. OC 1.64836

Log. cos  $\alpha$  1.24536

Log. ON 0.89372 ON = 7.8 mm.

Log. OC 1.64836

Log. cos  $\beta$  2.83813

Log. OP 0.48649 OP = 3.1 mm.

Log. OA' 1.17609

Log. sin  $\beta$  1.99897

Log. OQ 1.17506 OQ = 14.9 mm.

For Copper Sulphate.

$C = (100) : (0\bar{1}0) = 79^\circ 6'$

Acute  $\alpha = 82^\circ 16'$

Acute  $\beta = 72^\circ 34'$

Log. OA 1.17609

Log. cos C 1.27668

Log. OK 0.45277 OK = 2.8 mm.

Log. OB 1.62325

Log. sin C 1.99209

Log. OL 1.61534 OL = 41.2 mm.

OD = 39.0 mm.

Log. OD 1.59106

Log. sin  $\alpha$  1.99603

Log. OM 1.58709 OM = 38.6 mm.

Log. OC 1.64836

Log. cos  $\alpha$  1.12892

Log. ON 0.77728 ON = 6.0 mm.

Log. OC 1.64836

Log. cos  $\beta$  1.47654

Log. OP 1.12490 OP = 13.3 mm.

Log. OA' 1.17609

Log. sin  $\beta$  1.97958

Log. OQ 1.15567 OQ = 14.3 mm.

These values thus calculated were all marked off on the two drawings, the parallels and diagonals drawn, and then finally the proper lengths given to the axes  $a$  and  $c$  by multiplying the length of  $A''O$  and  $OC$  by the values of the  $a$  and  $c$  axial ratios. These proper lengths are  $aO$  and  $a'O$  in the case of the  $a$ -axis, and  $cO$  and  $c'O$  in the case of the  $c$ -axis. The  $b$  semi-axes  $Ob$  and  $Ob'$  are already of their correct unit length.

We shall next proceed to employ the triclinic axes of copper sulphate, as just drawn in Fig. 357, for the drawing of the crystal of that salt which forms the subject of Chapter XIX. In so doing the process of drawing triclinic crystals in general will be well illustrated.

**Copper Sulphate.**—The construction for the particular crystal considered in Chapter XIX., and which is typical of the greater number of the dozen crystals measured during the author's reinvestigation of copper sulphate, is shown in Fig. 359. Fig. 227 in Chapter XIX. (page 283) is a reproduction of the finished outline of Fig. 359, and with the faces marked with their form letters.

The prism edges are first drawn, parallel to the vertical axis. To get their positions, a section of the prism is made to represent the faces of  $p = \{110\}$  and  $p' = \{1\bar{1}0\}$ , by joining with thin lines the ends  $A, B, A', B'$ , of the  $a$  and  $b$  axes. Then the traces of the somewhat narrow  $a$ -faces are put in the section, beginning, say, with the front one, parallel to the  $b$ -axis and of the observed size (that is, at such a distance from

the centre as makes the section line of the  $a$ -face have about the right length relative to those of the  $p$ -faces on each side of it); next the back  $a$ -face is similarly inserted into the section, and the  $b$ -edges may also be introduced in like manner parallel to the  $a$ -axis, and so as to have about the right relative length. Then the pair of faces of  $p'' = \{1\bar{2}0\}$  are to be provided for in the section, parallel to the lines joining the intercepts  $2a$  and  $b$ , and of the proper observed relative size. Lines are then drawn parallel to the vertical axis to represent the prismatic edges, at present of indeterminate length, through all the corners of the section thus constructed.

Among the end-faces the two parallel  $o$ -faces are so predominantly developed, that it is simplest to assume at first that no other end-face is present, and to construct the  $o$ -faces accordingly. The outline of each of these faces will be seen in thin lines in the drawing. The zonal arrangement of the crystal, as clearly indicated by the stereographic projection, Fig. 228 of Chapter XIX., will help us greatly, and we see at once that the pair of  $po$  edges (for lettering of faces see Fig. 227, page 283, Chapter XIX., in which the construction lines are left out) must be parallel to the edges  $pt$  and  $to$ , for the faces  $p$ ,  $o$ , and  $t$  all belong to one and the same zone. We need only find by construction, therefore, the direction of any one of these edges, and that between  $p = (110)$  and  $t = (021)$  will be a convenient one to choose. The  $p$ -face may be represented by the line  $AB$ , joining axes  $a$  and  $b$ , and by lines through  $A$  and  $B$  parallel to the vertical axis. The plane  $t = (021)$  is represented by joining  $2c$  and  $B$  and drawing a line through  $2c$  parallel to axis  $a$ . This cuts the vertical line erected from  $A$  at the point  $P$ , and as the point  $B$  is also common to the two planes  $BP$  is the direction of their intersection. The edges  $pt$ ,  $to$ , and  $op$  will thus be parallel to  $BP$ . The direction of the last edge may easily be found in confirmation directly as follows: Join  $A'$ ,  $B$  and  $C$  to represent the plane  $o = (111)$ , and draw a line through the centre  $O$  parallel to  $AB$  to represent  $p = (\bar{1}\bar{1}0)$ , this cuts  $A'B$  at  $Q$ , and  $C$  being common to the two planes  $CQ$  is the direction of intersection of the  $p$ - and  $o$ -planes. It will be observed that  $CQ$  and  $BP$  are parallel, as they should be from the zonal relationships referred to, proving the parallelism of the edges  $po$  and  $pt$ , and consequently also of  $to$ .

The edges  $ao$ ,  $aq$ , and  $qo$  are all parallel to the line joining the axes  $b$  and  $c$  at unit intercepts, that is, to  $BC$ ; for the forms  $a$ ,  $q$ ,  $o$  all belong to the same zone. Similarly, the edge  $ac$  between the macro-pinakoidal  $a$ -face and the very small basal-pinakoidal  $c$ -face, is parallel to the axis  $b$  from its very nature, the edge  $ac$  having been chosen as  $b$ -axis. Again, the edges  $bt$ ,  $tq$ ,  $qc$  and  $cq'$  are all parallel to the axis  $a$ , for  $t$ ,  $q$ , and  $q'$  all belong to the pinakoidal zone  $[bc]$ , the possible edge between  $c$  and  $b$ , in this case modified by  $t$ ,  $q$ , and  $q'$ , having been chosen in the first instance as the  $a$ -axis.

The directions of the edges  $p'q'$  are next to be found. To represent  $p' = (1\bar{1}0)$  we draw lines parallel to axis  $c$  through  $B'$  and  $A$ , and to represent  $q' = (0\bar{1}1)$  we draw a line joining  $B'$  and  $C$ , and through  $C$  a line parallel to axis  $a$ ; this intersects the vertical from  $A$  at  $M$ , and  $B'$  being common to the two planes  $B'M$  is the direction of their intersection, and the edge  $p'q'$  is parallel thereto.

Similarly, we find the direction of the edge  $p''t'$  by finding the intersection of the

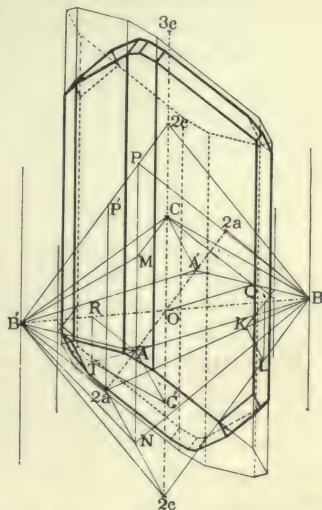


FIG. 359.—Construction of Measured Crystal of Copper Sulphate.

two planes  $p''=(1\bar{2}0)$  and  $t'=(0\bar{2}1)$ . For  $p''$  we join  $2a$  and  $B'$ , and draw a line through  $2a$  parallel to axis  $c$ , and for  $t'$  we join  $B'$  to  $2c$ , and draw a line through  $2c$  parallel to axis  $a$ ; this cuts the vertical from  $2a$  at  $P'$ , and  $B'$  being again common to the two planes  $B'P'$  is their intersection and the edge  $p''t'$  is to be drawn parallel thereto.

The intersection of  $p$  and  $s'$  is also required, as the direction of the edges  $ps'$ . It is readily obtained by drawing a plane to represent  $s'=(12\bar{1})$ , that is, joining the intercepts  $2a$ ,  $2c$  below, and  $B$ , and by dropping a line parallel to axis  $c$  from  $A$ , the line  $AB$  representing the prism  $p=(110)$ ; where this vertical cuts the line  $2a:2c$  at  $N$  is a point on the intersection, and  $B$  is common to the two planes. Hence  $BN$  is the intersection required, and the edges  $s'p$  are parallel thereto, as are also the opposite edges  $s'q'$  of the two  $s'$  faces.

It will be obvious that the edges  $bs'$  are parallel to the line  $KL$ , for  $K$  and  $L$  are two points on the intersection of the two planes  $b=(010)$  and  $s'=(12\bar{1})$ . Or we might have taken the line  $2a:2c$  itself as the direction of the intersection, for  $KL$  is parallel to it. The edge  $p''s$  is parallel to the line joining  $B'$  and  $2a$ .

The only other direction required for the drawing of the whole crystal is that of the edges  $p''o$ , which is clearly  $AT$ ; for  $o=(1\bar{1}\bar{1})$  is represented by joining  $B'$ ,  $C'$ , and  $A$ , and  $p''$  by joining  $B'$  to  $2a$ , then drawing a parallel to the latter line from  $A$ , cutting axis  $b$  at  $R$ , and another line  $RT$  parallel to the vertical axis from  $R$ .  $T$  is a point of intersection and  $A$  is common, hence  $AT$  is the line of intersection of the two planes.

In drawing a crystal of this kind, where the end-faces are developed to very different extents, and each face constitutes along with its parallel fellow at the other end a separate form, the chief difficulty is to give the various faces their observed relative dimensions. In this particular case, where the  $o$ -faces so largely predominate that it is most convenient to draw them in at first as the only end-faces, one proceeds, after having settled, as has now been done, the directions of all other edges on the crystal, to replace such of the edges between  $o$  and pinakoidal or prism forms as are modified on the actual crystal, by the smaller end-faces, beginning conveniently with the upper  $s$ -face and then following on with the  $t$ ,  $q$ ,  $c$ ,  $q'$ ,  $t'$ , and  $s'$  faces, after which the lower faces of these forms can be similarly proceeded with.

After having completed the drawing of a crystal, especially of a somewhat difficult triclinic one such as that of copper sulphate, the drawing should be carefully examined alongside the stereographic projection (Fig. 228, page 283, Chapter XIX. in this case), in order to verify that those faces belonging to one and the same zone, whenever they touch, are bounded by edges parallel to one another and to the zone axis. Such an inspection gives confidence that the drawing has been accurately carried out.

Another drawing (already referred to) of a triclinic crystal, of the substance methyl triphenylpyrrholone, of a more general and easier type, with the faces more evenly developed, is given in Fig. 47, page 98, Chapter VI. (without construction lines, which have been erased for the sake of clearness), alongside its stereographic projection, Fig. 48, and this drawing can also readily be examined in the sense just indicated. The relations of the three primary pinakoids  $a$ ,  $b$ , and  $c$  are here of the usual character, the goniometrical angles  $ab$ ,  $bc$ , and  $ac$  being all less than  $90^\circ$ , whereas in the case of copper sulphate the angle  $bc$  was just over  $90^\circ$ . The pro-



cedure for the drawing of the crystal is practically the same in both cases, however, the axes being first drawn as in Figs. 357 and 358, and then the various faces inserted from the knowledge either directly of their intercepts or after determinations of their intersections with each other, as in the case of the copper sulphate crystal now worked out in detail.

The drawing of all the various types of crystals has now been discussed, and from the experience of the general principles of the construction gained with the typical cases considered, it should be possible to carry out any crystal drawing without difficulty. The case of twin crystals will be specially considered in the chapter (XXVIII.) relating to twinning.

The great value of the stereographic projection has again been abundantly emphasised in this chapter, and its importance as an aid to crystal drawing, so strongly urged by Penfield, been rendered very obvious. It has been shown, indeed, that in many cases the use of it renders the general method of intersections unnecessary, but it is well, all the same, that the latter should be thoroughly understood, and the applications of it in this chapter must have brought out very clearly, and fixed them indelibly on the memory, the fundamental relations of axes, intercepts, indices, and crystal elements, in crystals of the various types of symmetry.

A mode of drawing crystals in this now universally employed clinographic projection (or parallel-perspective, as it is often called) without having first to construct the crystal axes, from a gnomonic projection with the intermediate aid of an orthogonal projection, will be described in Chapter XXVII. after the description of the gnomonic projection.

## CHAPTER XXVI

### GONIOMETRY AT TEMPERATURES HIGHER AND LOWER THAN ORDINARY

THE effect of change of temperature on crystals is to bring about a homogeneous deformation, not permanent in the sense used in Chapter XXIX. in connection with the movement along glide-planes, but only persisting as long as the temperature remains constant at the new level. It will be clearly apparent that change of temperature must affect the forces which hold the structural units together, so that not only the exterior shape of a crystal but also the homogeneous internal arrangement of the structural units (to be dealt with in Part II.)—be they considered as the chemical atoms, molecules or groups of molecules, or Sohnckian points representing them—must be a function of the temperature. This homogeneous deformation is of such a nature, however, that the symmetry of the crystal, the mutual relations of the forms it displays, and the law of rational indices which connects them, are all quite independent of it. In the most general case of a triclinic crystal the dilatation induced by change of temperature varies with the direction within the crystal, and there may even be contraction along certain directions while expansion occurs along others. The net effect, however, is usually for an increase of volume to accompany rise of temperature and a diminution in bulk to follow cooling. The exact laws which have been found to govern the dilatation of crystals belonging to the various systems of symmetry will be discussed in a subsequent chapter (LVI.), but it will be obvious that they will in general lead to alteration of the crystal angles, and we must therefore be provided in the laboratory with a means of measuring such changes of angular magnitude in order to complete our goniometrical study of a crystallised substance. They are always relatively very small within the limits of the temperature intervals corresponding to the lives of crystals, that is, within which the crystals may be preserved intact as solid chemical substances, without any trace of fusion, volatilization, or chemical decomposition. The angular changes have never yet been found to exceed a very few minutes of arc.

For the measurement of crystal angles at temperatures higher than the ordinary it is necessary to employ a goniometer constructed on a somewhat larger scale than the excellent instruments for ordinary temperature work described in Chapter III. For although sometimes, as in the

case of gypsum (selenite), the changes brought about in the crystal angles by a rise of temperature of  $100^{\circ}$  C. amount to four or five minutes, such cases are exceptional and the changes rarely reach a single minute, and often indeed only amount to a few seconds. Hence the goniometer which is employed must read to seconds. The No. 2*a* Fuess goniometer and the similar Troughton and Simms horizontal-circle goniometer described in Chapter III. read to half minutes, a fineness which is quite adequate for measurements at the ordinary temperature, the readings being usually only required to the nearest whole minute. For the perfection of formation of the crystal faces is only very rarely indeed of higher degree than to permit those angles which are of equal value as regards the symmetry to agree among themselves to within one or two minutes, and the crystallographer considers himself fortunate when he obtains crystals exhibiting this perfection of facial planeness. Hence a larger instrument reading to seconds is not only of no more use in ordinary crystal measurements than the two excellent goniometers referred to, but is positively a drawback, as it must of necessity be larger in order to include a larger and more finely divided circle, and therefore heavier, less handy, and more tiring to manipulate, besides absorbing more time in an equal number of measurements. But for work at higher temperatures up to  $200^{\circ}$  C. Fuess constructs an admirable larger goniometer, No. 1*a*, which is also an excellent instrument for the measurement of refractive indices by the method of the  $60^{\circ}$  prism to be described later in Chapter XLVI. It is shown in Fig. 360 on the scale of one-sixth its size, and a section of its axial system is added in Fig. 361.

The fixed outer cylinder *a*, in which the axes of the rotatable circle and the adjustable crystal holder successively rotate, is rigidly supported by a strong tripod *b* furnished with levelling screws. Its boring is cylindrical in its central part but conical above and below, in order to support the circle axis *c* within it. The circle in this instrument is a simple uncovered circular plate *d*, adequately stout to resist deformation, and carried at the head of the axis *c*, which is capable of rotation in the cylinder *a* by means of the large milled head *e* or the ring *f* carried rigidly below it, which is added for the greater convenience of rotation by the hand. The circle may be clamped to the outer fixed cylinder and tripod by means of the screw *g*, and finely adjusted by an adjacent screw *h* at right angles to *g* in a manner which will be clear from the figure. The axis *c* is hollow within, with a boring cylindrical for its greater part, but conical at the top, and within it there rotates a second axis *i* shaped to fit the boring and capable of being rotated from its lower termination by the milled head *j*. This axis carries the crystal centring and adjusting apparatus, of like construction to that of the goniometer No. 2*a* but larger; it is not carried directly by *i*, but by a solid steel cylindrical innermost axis *k* having a screw thread cut on its lower portion, so that it may be raised or lowered by means of the milled head *l* of a flanged driving-nut, in order to bring the crystal carried at the head of the adjusting apparatus to the exact level of the common optic axis of the telescope and collimator, the steel axis being keyed to prevent rotation otherwise than along with *i*. This latter axis *i* can be clamped to the circle axis by the screw *m*, and finely adjusted to the circle by means of the adjacent fine adjustment screw *n* at right angles to *m*.

The collimator and telescope are supported similarly and independently about the exterior of the fixed outer axis *a*, in such a manner that both are free to move round the circle and to be fixed and finely adjusted in any desired position with respect either



to each other or to the circle. Indeed the two optical tubes *o* and *p* are similar in all respects, so that either may be used at will as collimator or as telescope, an eyepiece *q* or a signal-slit *r* being inserted accordingly at the outer end of the tube, the objectives *s* at the inner ends being alike. In Fig. 360 the right optical tube is shown arranged as telescope, and the left as collimator, to which latter the lengthening illumination tube *t* is also attached. Each optical tube is supported on a stout column *u* arising from the end of an arm *v* or *w* radiating from and solid with a stout ring surrounding the fixed axis *a*, the arm being continued on the other side into a counterpoise *x* or *y*.

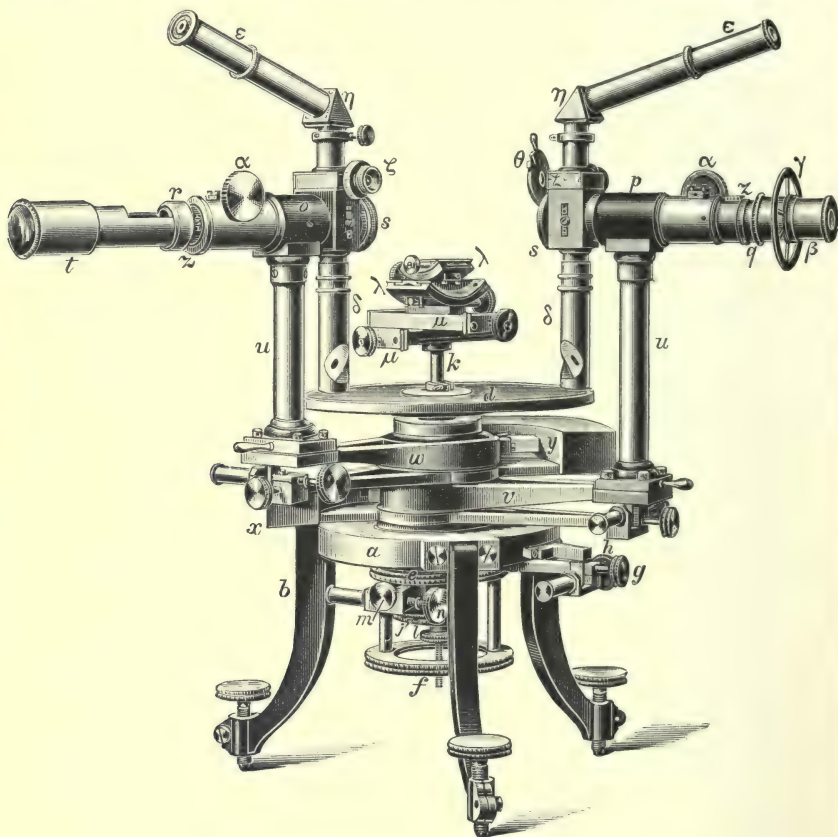


FIG. 360.—No. 1a Fuess Goniometer.

Each arm carries beneath it a fixing and a fine adjustment screw, in order that either or both of the optical tubes may be adjusted to any desired position about the circle and fixed there. The signals and eyepieces are similar to those of the No. 2a model, and are arranged to fit in automatic adjustment by means of the notched tightening collar *z*, which gears with a little V-shaped projection carried by a collar on the signal or eyepiece; a rack and pinion movement, manipulated by the milled head *a*, is provided, which enables the last refinement of focus to be attained. If it be desired to employ polarised light, as is essential in refractive index determinations, a Nicol prism *β* may be attached in front of the eyepiece, the prism being provided with a finely divided circle *γ*. A pair of such Nicol prisms are provided, corresponding to

the duplicate eyepieces, to meet the eventuality of one being required on each optical tube. Two much larger Nicol prisms, mounted on circles of considerable size, reading on silver arcs with the aid of a vernier in each case to single minutes, are also provided for attachment in front of the objectives of the two optical tubes, for use in certain optical observations to be described later, for which such a position of the polariser or analyser is preferable. A Babinet compensator (see Fig. 836, Chapter LII.) can also be attached in front of one of these large Nicols.

The circle is divided on its silver annulus (inlaid nearly flush with the surface of the circle plate) directly to every  $10'$ , and is read by two micrometer microscopes  $\delta$ , one of which is carried by each of the optical tubes, near the objective, in a manner which will be clear from Fig. 360. The objective part of each microscope  $\delta$  is fitted below the objective end of the telescope, and terminates below in an oblique diaphragm with central aperture, enamelled white in order to reflect diffused light on to the graduations of the circle, the silver annulus bearing them on its horizontal surface being immediately below the aperture. Above the telescope tube and immediately over the tube  $\delta$  a micrometer  $\zeta$  is fitted, the drum of which is divided into 60 parts; as one revolution corresponds to the movement of the parallel pair of spider-lines from the position in which one graduation of the circle is set symmetrically between them until the next graduation is similarly set, each division of the drum corresponds to ten seconds, and the tenths of a division, corresponding to one second, can be estimated. The very low power eyepiece  $\epsilon$  is not arranged vertically over the objective tube of the microscope as usual, but is inclined so as to bring it more conveniently near the observer's eye, just above the eyepiece of the telescope, the rays from the objective being directed into it by means of a totally reflecting prism  $\eta$ .

On the author's instrument a small tubular electric glow-lamp is fixed opposite the inclined white diaphragm at the bottom of  $\delta$ , and a switch for it is fitted on the mahogany basal plinth on which the instrument stands, over which fits a glass protective shade covering the whole instrument when not in use. The light can thus be switched on momentarily for the reading of the circle, and extinguished immediately afterwards for the observation of the signal-image reflected from the crystal face or refracted through the prism, according as crystal angles or refractive indices are being measured. These arrangements will be clear from Fig. 363, which represents the No. 1a goniometer in actual use by the author for higher temperature measurements.

An additional lens  $\theta$  is provided, to be fitted before the objective of the optical tube used as telescope, in a manner which permits of its being instantly swung in or out of position, to convert the telescope into a low power microscope for the observation and adjustment of the crystal, as in the No. 2a model.

The crystal-adjusting and centring apparatus, lettered respectively  $\lambda$  and  $\mu$ , is similar to that provided with No. 2a, but larger.

The heating apparatus for bringing the crystal to the required temperature is shown in partial section in Fig. 362 (in elevation above and in plan below), and in position in Fig. 363. It consists of a spherical double-walled air-bath of copper  $a$ , continued at opposite sides into horizontal cylinders  $a'$ , along the interior of each of which runs a stout copper rod  $b$ , terminating at the inner end in a shallow copper cup  $c$  concentric with the walls of the bath, and at the outer end projecting free

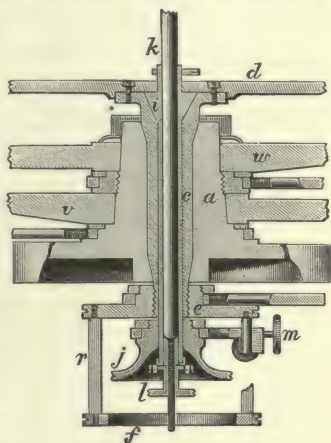


FIG. 361.—Section of Axial System of No. 1a Goniometer.

sufficiently far to enable it to be heated by a special form of Bunsen gas lamp *d* with fan-shaped burner. All the space within the cylinder not occupied by the rod is filled up with asbestos, as is also the space between the outer and inner spheres forming the air-bath. The heat communicated to the ends of the two rods by the Bunsen flames is conducted to the air-bath, and if the burners are nicely regulated to afford approximately the same heating effect the air-bath becomes very evenly raised in temperature. The heat is warded off from the goniometer by the tin-plate screens *e*, and the cylinders are wrapped round with thick felt to prevent undue radiation. The apparatus is supported near the outer ends by two semicircular rests *f*, each forming the upper termination of an adjustable column carried by a tripod base, these two supports being adequately compact to stand conveniently on each side of the goniometer, when the apparatus is in position over the latter, without interfering with the manipulation of the instrument. Besides being adjustable itself for height the column carries an adjustable arm which bears the Bunsen burner at its end, so that the burner may be delicately adjusted for distance below the rod which it heats; the

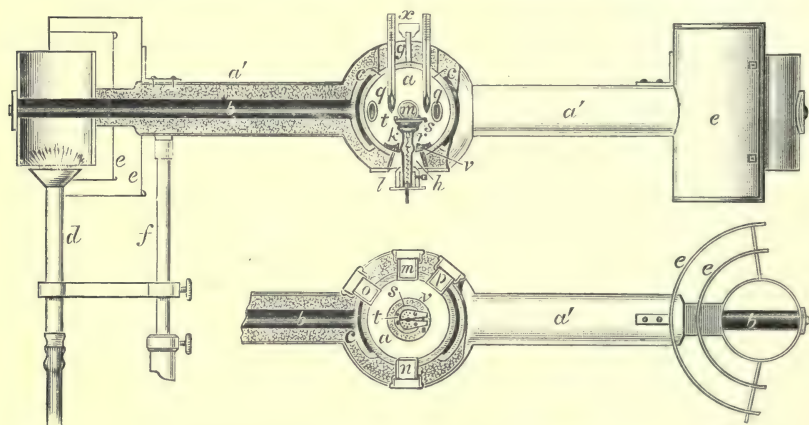


FIG. 362.—Crystal-heating Apparatus of No. 1a Goniometer.

size of its horizontally elongated flame—which latter rarely requires to be more than half an inch high for the highest temperatures which crystals and the instrument itself will safely withstand (that is, not exceeding  $200^{\circ}$  C.)—is regulated by a screw pinchcock on the indiarubber gas-supply tubing just below where it is attached to the burner.

The air-bath has two circular openings vertically above and below one another, the vertical diameter of the sphere passing through the centre of each. The upper opening is of sufficient size to admit the two thermometers through the similarly constructed copper and asbestos plug *g* which closes it, but the lower aperture *h* is only just large enough to allow the special crystal holder *k* to pass through it, with sufficient play to prevent contact during rotation of the goniometer circle and the crystal holder *l* which moves with it. The air-bath requires to be placed so that its vertical diameter is as nearly as possible coincident with the goniometer axis. It is pierced with four side windows in the case of the author's instrument (one more than usual), each filled with truly plane and parallel-surfaced glass plates. Two, *m*, *n*, are placed opposite each other at the extremities of that horizontal diameter which is perpendicular to the direction of the cylinders and rods, so that when the collimator and telescope are arranged in the same straight line with one another (also at right angles to the heating apparatus between them) the Websky signal of the collimator



can be seen through the telescope and the windows; the other two windows, *o*, *p*, are arranged one on each side of the front window *m* (the one nearer to the telescope of the two just referred to), at angles of  $55^\circ$  and  $40^\circ$  to the latter respectively. The instru-

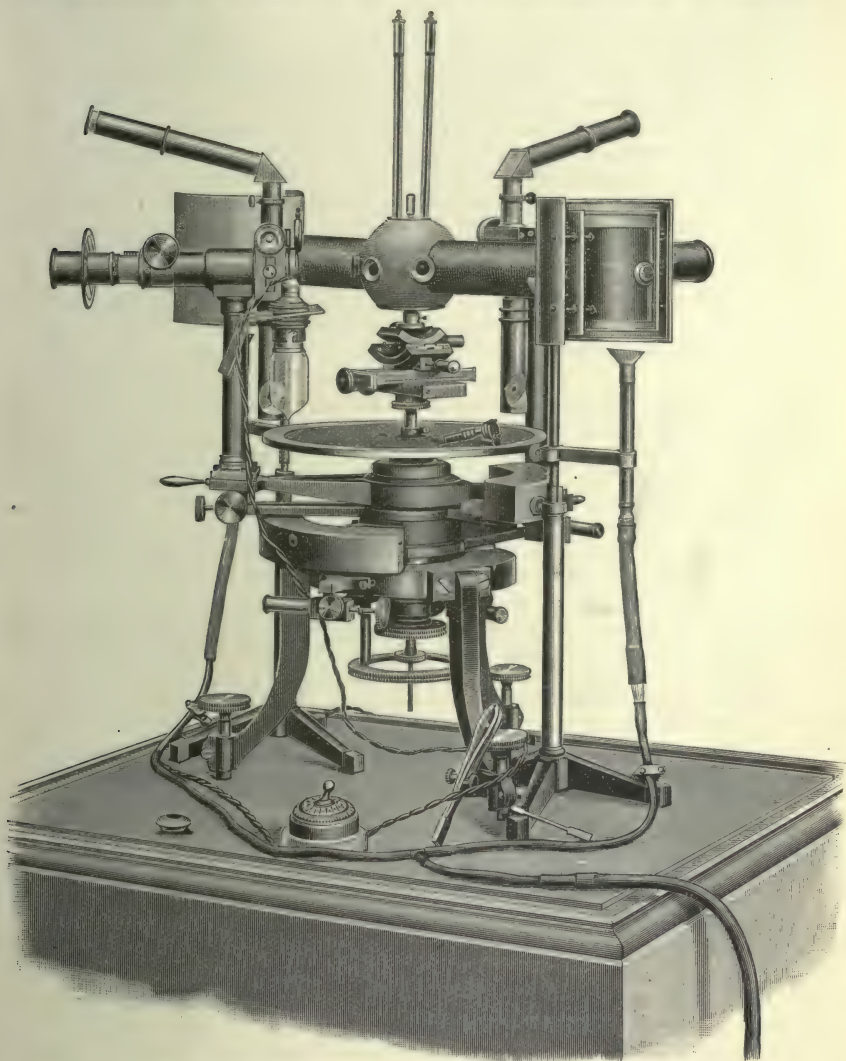


FIG. 363.—No. 1a Goniometer with Crystal-heating Apparatus in Position.

ment as supplied by Fuess has only one of these at about  $55^\circ$ , but this angle has been found inconveniently large by the author when determining the angle of minimum deviation with a  $60^\circ$  prism, except for substances of very high refraction, although it is quite convenient for crystal angle work. With two windows at  $55^\circ$  and  $40^\circ$  practically all cases are provided for. There is not room to cut both on one side, so one is cut on each side of the front central window.

The crystal holder is a special feature. There fits first into the socket at the top of the crystal-adjusting and centring apparatus the peg of a second and more widely socketted fitting *l*, into which fits the crystal holder proper *k*. The tubular stem of the latter is of metal in its lower half but of glass in its upper half, in order to prevent conduction of heat from the crystal; the latter would otherwise never quite attain the temperature of the bath as indicated by the thermometers, the bulbs *qq* of which are brought quite close to the crystal on each side. The glass part is of narrow glass tubing, which is blown out into a bulb just above the level of entry into the interior of the bath; it is again expanded at its upper termination into a shallow cup *r*, in which rests a slightly larger metallic button *s*, spherically shaped below with the same radius of curvature as the cup, so as to be capable of adjustment in the cup in any direction. The button carries above a miniature adjustable vice *t* for gripping the crystal, either directly or with the intervention of a little crystal holder which one can make for oneself out of stout platinum foil to suit the particular crystal and which can be held in the vice, one jaw of which is fixed to the button while the other is only pinned to the button and can be adjusted with reference to the fixed jaw by means of a screw, so as to grip anything inserted between. The button and all that it carries is kept pressed down on its cup by means of a spiral spring attached to the button below its centre, and which passes down through the glass tube and its metallic continuation in a stretched condition to a hook screwing in a nut which forms the lower termination of the tube and which has the same diameter as the outside of the tube, so that it forms no impediment to the fitting of the latter in the socket. The whole holder, removed from its socket, is shown lying on the circle plate in Fig. 363. After its insertion in the socket this special holder can be clamped there by a side screw, manipulated by a key supplied for the purpose, and which also fits and manipulates the screw of the crystal-holding vice. This key is shown, leaning against the tripod of the right pedestal of the heating apparatus, in Fig. 363. It is obviously impossible to use any form of wax for attaching the crystal, as it would melt when the temperature was raised. Each jaw of the vice is pierced by a number of vertical holes for the reception of a little hard-metal pin, which may be fixed in the most convenient of the holes to enable the crystal to be gripped between the two upright pins, the screw manipulated by the key regulating the tightness of the grip. If, however, the shape of the crystal does not lend itself to being held in this manner during the measurements, the platinum foil holder already mentioned may be used and the pins discarded. A number of such little pincettes of strong platinum foil should be kept ready, of different sizes to suit different crystals; the two prongs of the pincette can be bent in any way which is desirable for the better gripping of the crystal, and the lower part of the holder, where the platinum strip has been bent on itself at its centre so as to form the pincette, is to be held directly between the jaws of the vice.

For convenience of inserting this special glass-stemmed crystal holder in the socket fitting, which replaces the ordinary crystal holder, when the bath is in position, a pair of spring tongs are provided, shaped at their ends so as to grip the button-head of the holder while avoiding the glass cup. They are shown in Fig. 363 leaning against the right-front foot of the goniometer tripod. The aperture at the base of the air-bath should first be closed by a little slate washer *v*, shown resting on the mahogany base, in front to the left, in Fig. 363; it is shaped below to the curvature of the bath and has a central hole of the right size to permit the glass stem but not the bulb to pass freely; it is placed loosely inside the bath before lowering the holder into position with the tongs. During rotation of the goniometer circle together with the holder and its crystal any play of the stem due to slight imperfection of centring is still permitted by the loose slate annulus, whilst the bath is at the same time effectively closed.

When the crystal has been mounted on the holder and the latter is

ready for being placed in the bath for the measurements, the bath itself is first adjusted on the stirrups of its two supporting columns at the height which brings the windows opposite the optical tubes, that is, so that the horizontal axis of the bath and its cylindrical prolongations and the optical axis of the collimator and telescope (arranged in the same straight line for direct vision of the signal) intersect each other at approximately right angles, and so that the point of intersection also lies on the vertical axis of rotation of the goniometer, which latter axis then passes through the centre of the basal and upper apertures of the bath. The centre of the socket for the crystal holder should then be properly centred, so as to remain apparently immovable on rotation of the circle and all that it carries, when regarded from above through the upper opening of the sphere, the slate annulus being absent during this centring. The final adjustment of the bath is at once attained after this by making the socket occupy the centre of the lower aperture of the bath, as seen from above. The annulus is then placed in position in the bath, and the crystal holder inserted through it into the socket with the aid of the tongs, and gently clamped by the screw.

The crystal should obviously have been mounted, either between the two pins of the vice or in one of the platinum pincettes held in the vice, so that the zone of faces the mutual inclinations of which are to be measured, or the two faces which form the prism the angle and refractive minimum deviation of which are to be determined, will be approximately adjusted parallel to the goniometer axis when the holder is fixed in its socket. The goniometer observing lamp is now switched on and the images of the collimator signal reviewed in the telescope. Further adjustment will in general be required, and this is done by gently pressing down that side of the adjusting button in its glass cup which experience shows causes the signal-image under observation to come towards the centre of the field, with the end of the rod-shaped key for the vice and socket screws, this key being just conveniently shaped and long enough for the purpose. The image from the next face should then be observed, and if any adjustment be required it must be done by pressing down that side of the button which is both about  $45^\circ$  from the side formerly depressed and which causes this second image in question also to come to the centre; if the pressure be properly directed the first adjusted face will then only move in its own plane and its image will consequently not be put out of adjustment again. Of course adjustment by hand in this way, by pressure on the button with the key-end, will not be perfect on the first attempt, but only one or two approximations ought to be necessary in order to adjust almost perfectly the edge between the two crystal faces and their whole zone, without having recourse to the adjusting segments of the goniometer until the last moment, when a mere touch of one or both of them will perfect the adjustment. Any considerable use of the segments is very inconvenient, as it renders the glass stem of the special crystal holder oblique and puts the crystal seriously out of centring, so that it may not remain visible through the windows on rotation; for this crystal holder is necessarily much longer than the



normal crystal holder for the centring of which the movements are calculated.

The stopper may now be inserted by means of its handle-knob  $x$  in the top of the air-bath, and the two thermometers placed in the two holes drilled for their passage through the stopper. These holes are lined with cloth or soft paper, to prevent contact of the glass stems of the thermometers with the metal. Care must be taken that the crystal has been so well centred that on rotation it does not touch the thermometer bulbs, which are arranged at its level, and as close as may be to the crystal, and the stopper itself must be rotated, if necessary, so that the bulbs are not in the way of the passage of the light rays between the collimator, crystal, and telescope. Presuming now that crystal angles are to be measured (refractive indices will be dealt with in Chapter XLVI.), the collimator should be fixed so that the light from it passes normally through the back window of the spherical bath, and the telescope should be directed at the side window which is inclined  $55^\circ$  from the front window parallel to the back one, so that the two optical tubes are inclined at about  $125^\circ$ , a very convenient angle for the observation of the signal-images reflected from the adjusted faces. (In the case of refractive index determinations the window at  $40^\circ$  on the other side is used as a rule, and this is the case actually shown in Fig. 363, as it was the one which revealed the details of the goniometer to greatest advantage.)

Before lighting up the Bunsen lamps the angle or angles to be measured at higher temperatures should first be measured at the ordinary temperature as recorded by the thermometers, both of which should have recently had their fixed points verified or corrected. The angle or angles will already be known to minutes, from the ordinary goniometrical investigation, but the measurements now require to be carried out to seconds. The last signal-image observed should be left adjusted to the vertical spider-line, in order that it may be observed from time to time during the heating operation, so as to verify that there is no sudden disarrangement owing to cracking of the crystal or other disturbing cause. It should move steadily away from the spider-line parallel to itself during the heating if all goes well.

All being now ready for the determination, the two Bunsen burners are lighted. The fan-shaped flat nozzles enable the flames to be checked down, by the pinchcocks on the caoutchouc gas-supply tubing, to narrow low strips of flame about an inch long, which should be adjusted exactly under the rods. This enables the heating to occur very slowly and deliberately. The author finds a "Stott" governor to be of considerable use in preventing sudden fluctuations of the gas supply; it is inserted between the gas-supply tap and the burners. The supply tap is turned fully on, and the gas passes thence by a short length of indiarubber tubing to the governor, thence another short length of tubing delivers the gas to a second gas tap fitted with a long lever arm moving over a quadrant graduated in degrees, which enables the amount of gas delivered to the burners to be regulated to a nicety. From this fine adjustment tap a further short length of caoutchouc tubing conducts

to a metallic T-piece, where the gas divides and is conducted to the two burners, as shown in Fig. 363, by separate indiarubber tubes of equal narrow bore, each fitted with a screw pinchcock, as already mentioned, near the burner in order to obtain any necessary separate control of either flame, in case the thermometers are not found to indicate an equal rise of temperature on each side of the air-bath. The rise should be carefully watched, and the flames regulated so that the temperature moves deliberately up to the required height, where it eventually attains constancy. With the aid of the governor it is easy to attain a constant temperature for a particular position of the lever arm of the tap on the graduated arc, and for an interval of time which is ample to enable the determination of the angles between the faces of a complete zone to be carried out in duplicate; and also, as will subsequently be shown, for a complete duplicate set of determinations of the minimum deviation by a  $60^\circ$  prism to be made for a numerous series of wave-lengths of light, as well as repeated measurements of the angle of the prism. The illuminating light for crystal angles or the angle of a prism is, of course, the ordinary white light of the goniometer lamp; but for refractive index determinations of minimum deviation the spectroscopic monochromatic illuminator is employed in the manner detailed in Chapter XLVI.

As soon as constancy at the required temperature is attained, the steady movement of the signal-image having correspondingly become arrested, the measurement or measurements of the crystal angles are carried out just as were those for the ordinary temperature. The measurements should be repeated, and if there be any slight difference a third set of readings should be taken in confirmation. When two series of identical readings have been obtained to within two or three seconds at most, the measurements may be accepted as representing the truth for this temperature, and as proving that the temperature indicated by the thermometers has actually been attained by the crystal.

With this apparatus measurements of crystal angles (or refractive indices) can be very efficiently carried out for temperatures up to  $200^\circ\text{C}$ . Higher than this it is not advisable to go, as injury to this excellent, delicately accurate, and very costly goniometer might occur.

**Goniometry at very High Temperatures.**—A few of the more important angles of quartz and calcite have been measured by F. E. Wright<sup>1</sup> at temperatures considerably higher than  $200^\circ\text{C}$ ., with the aid of a special accessory to a Goldschmidt two-circle goniometer (see next chapter, page 453). It is a kind of electric furnace, enabling temperatures up to about  $1150^\circ\text{C}$ . to be attained, and is shown in vertical section in Fig. 363a. The heating portion consists of two flat discs or cakes of alundun (fused bauxite, hydrated alumina)  $C_1$ ,  $C_2$ , 7 cm. diameter and 5 mm. thick, one just above and one immediately below the crystal, and on the inner side (that near the crystal) of each of which a spiral of 1.75 mm. pitch is grooved out; into this groove the heating platinum wire is wound and then covered with a layer of alundun cement and baked at  $1200^\circ$ – $1300^\circ\text{C}$ . These discs are backed by magnesia powder M, and mounted in a

<sup>1</sup> *Journ. Washington Acad. Sci.*, 1913, 3, 396.

hollow cylindrical water jacket constructed in two parts,  $A_1$ ,  $A_2$ . The edges of the cakes are shielded from direct contact with the cold water jacket by asbestos packing, and asbestos is also freely used to shield the nearer parts of the goniometer from the hot furnace. An asbestos ring  $B$ , and segments of alundum  $a$ , are so arranged in the space between the upper and lower parts of the water jacket, at the level of the crystal  $I$ , as to permit of the ready observation of the latter.  $S$  is the intake for the circulating cold water,  $F$  is one of the entering furnace wires of platinum, and  $D$  is the support by which the furnace is attached to the goniometer.

A current of 5 ampères at 110 volts is sent through the platinum wire

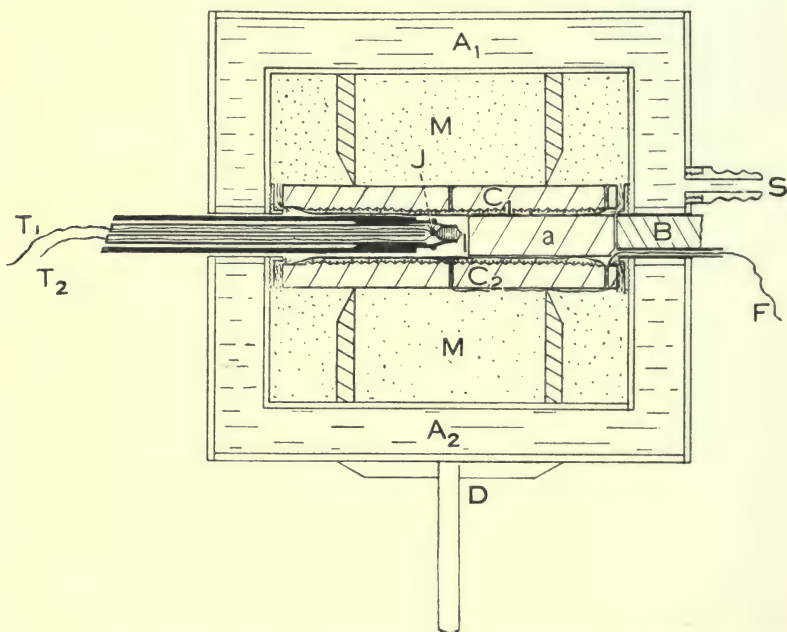


FIG. 363a.—Wright's Apparatus for High Temperature Goniometry.

for the production of the high temperature limit of  $1150^{\circ}\text{C.}$ , the actual temperature being determined by means of a thermo-element  $J$ , the thermal junction of which is in direct contact with the crystal;  $T_1$ ,  $T_2$  are the wires from the thermo-element leading to the potentiometer-galvanometer. The crystal holder naturally requires to be of a special character for this high temperature work, and takes the form of a porcelain tube on the end of which platinum jaws are mounted, in which the crystal is gripped and adjusted before the furnace is built up. The porcelain tube also serves for the admission of the wires  $T_1$ ,  $T_2$  of the thermo-element, which are enclosed in a couple of much finer porcelain tubes passing through the larger one. The adjustment of the crystal has to be carried out by hand, which imposes a considerable limitation on the measurements which are possible.



In the work on quartz and calcite the crystal was first measured at the ordinary temperature, as far as the limitations permitted; then the furnace was heated to a definite temperature, and the latter kept constant for a sufficient length of time to enable the crystal to be remeasured. This was repeated for each of the temperatures for which measurements were desired, up to  $1150^{\circ}$  C. Readings were made to quarter minutes of arc. At the higher temperatures the light from the furnace was so intense, even when screened as much as possible by a blue filter, that an electric arc was necessary for the illumination of the signal.

In the case of **quartz**, from the position angles (polar distance and azimuth, see next chapter) measured, the angle between the unit rhombohedron faces  $\{100\}$  over the pole for the different temperatures was calculated, and its semi-values are given in the following table. The angle of which the values are given is  $(100):(111)$ , the half of the angle  $rr' = (100):(122)$ , or in Bravais-Millerian notation  $(10\bar{1}1):(1\bar{0}11)$ .

Angle at	$0^{\circ}$ C.	$51^{\circ} 47' \cdot 4$	Angle at	$400^{\circ}$ C.	$51^{\circ} 42' \cdot 1$
„	$100^{\circ}$	$51 46 \cdot 4$	„	$500^{\circ}$	$51 39 \cdot 8$
„	$200^{\circ}$	$51 45 \cdot 1$	„	$550^{\circ}$	$51 38 \cdot 0$
„	$300^{\circ}$	$51 43 \cdot 8$	„	$575^{\circ}$	$51 36 \cdot 7$

For an increase of temperature from  $0^{\circ}$  to  $575^{\circ}$  C., therefore, the angle  $(100):(111)$  diminishes by  $10' \cdot 7$ .

At the temperature  $575^{\circ}$  the curve drawn to express these results, taking interfacial angles as ordinates and temperatures as abscissæ, exhibits a marked discontinuity. This is probably due to the conversion of the ordinary form of quartz, which may be termed  $\alpha$ -quartz, into a second variety which has been termed  $\beta$ -quartz, an account of which will be found in Chapter LV, under the heading of pseudosymmetrical polysymmetry. At the inversion temperature of  $575^{\circ}$  the signals reflected from both the rhombohedron and prism faces became wider and indistinct, and on regaining their sharpness had shifted their positions considerably. Up to this point the curve is of an ordinary exponential form, very similar to the curves representing the total expansion, specific volume, birefringence, and circular polarisation of quartz.

**Calcite** was found to behave normally, affording a curve which is practically linear up to  $600^{\circ}$  C., beyond which, and completely at  $700^{\circ}$ , the crystal decomposes into carbon dioxide and opaque calcium oxide. The cleavage angle—that of the primary rhombohedron over its polar edges,  $(100):(001)$ , and which is  $74^{\circ} 56'$  at the ordinary temperature ( $74^{\circ} 55'$  in the specimen used in the experiments)—proved to be  $75^{\circ} 52'$  at  $600^{\circ}$  C., the angle thus changing for  $600^{\circ}$  rise of temperature to the extent of practically a whole degree.

**Goniometry at very Low Temperatures.**—Passing now to the measurement of crystal angles at temperatures lower than the ordinary, V. M. Goldschmidt<sup>1</sup> (Christiania) has carried out a series of measurements on crystals of sulphur, calcite, and quartz at the temperatures of solid carbon dioxide and liquid air, namely, at  $-72^{\circ}$  and  $-175^{\circ}$  C., with the aid of a special cooling bath fitted to the No. 2 Fuess goniometer. It is shown

<sup>1</sup> *Zeitschr. für Kryst.*, 1912, 51, 1.

in Fig. 364 in vertical section. It consists of an open cylindrical vessel A, 81 mm. high and 56 mm. in diameter, within which a vertical tube B,

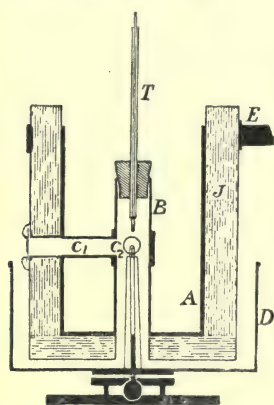


FIG. 364.—V. M. Goldschmidt's Apparatus for Low Temperature Goniometry.

12 mm. wide, penetrates centrally from below, forming the chamber inside which the crystal holder is enclosed. At a height of 30 mm. above the base of the cooling chamber two mutually rectangular horizontal tubes,  $C_1$ ,  $C_2$ , 5 mm. wide, radiate from the inner tube and pass out through the walls of the outer bath. They are closed by plate-glass windows, and serve for the illumination of the crystal by the collimator and the observation of the latter's signal by the telescope. The walls of all these tubes are very thin, in order to minimise the conduction of heat from outside. The tube B is closed above by a cork, through which passes the thermo-element enclosed in a glass tube T, with the thermal junction of the element arranged just above the crystal. The outside of the metal vessel A is surrounded by three successive isolation coats J, consisting respectively of 6 mm. of felt and paper, 2 mm. of cloth, and, outside all, 6 mm. of varnished paper. The chamber is closed by a thick felt cover, and is supported by the arm E of a rigid stand. Outside the lower half, nearly up to the tubes  $C_1$ ,  $C_2$ , a cylindrical leaden dish-screen D is arranged, which serves as an outer bath of the very cold air which falls out of the tube B; without it the lowest temperatures, about  $-175^\circ$ , could not have been attained.

A curious difficulty was experienced with the wax of the crystal holder, when liquid air was employed in the vessel A. It became so brittle that it fell to powder. The difficulty was overcome by mixing the wax with vaseline, and adding a protective outer layer of vaseline. For vaseline becomes hard but does not disintegrate under the influence of low temperature.

In using the apparatus the vessel A was filled to the brim with either solid carbon dioxide mixed with alcohol, or with liquid air. A temperature of  $-186^\circ$  C. was obtained in the outer bath, and of  $-175^\circ$  at the crystal, when liquid air was used;  $-72^\circ$  was the average temperature when the alcohol and carbon dioxide mixture was employed.

The results for the rhombic crystals of **sulphur** were as under in the case of four principal angles:

Angle.	+ 20 C°.	- 72°.	- 175°.
(100) : (110)	39° 7' 19"	39° 8' 35"	39° 10' 58"
(001) : (011)	62 17 18	62 23 21	62 29 50
(111) : ( $\bar{1}\bar{1}\bar{1}$ )	73 35 14	73 39 32	73 45 48
(113) : ( $\bar{1}\bar{1}\bar{3}$ )	90 19 39	90 32 49	90 45 41

The angular change in the case of the last angle is thus no less than  $+26' 2''$ .

The axial ratios  $a : b : c$  calculated for the three temperatures were as follows :

	$a.$	$b.$	$c.$
For $+20^\circ$	0.8133	1	1.9038
$-72^\circ$	0.8139	1	1.9120
$-175^\circ$	0.8151	1	1.9208

Using Sir James Dewar's values for the density at  $+17^\circ$  and  $-175^\circ$ , namely, 2.0517 and 2.0974, the topic axial ratios have been calculated for the rhombic space-lattice cell dimensions and found to be :

	$\chi$	:	$\psi$	:	$\omega$
For $+20^\circ$	1.7578		2.1612		4.1145
$-175^\circ$	1.7423		2.1375		4.1057

Thus all three of the cell dimensions diminish as the temperature descends.

The results for **calcite** were that the rhombohedron angle  $(100) : (010)$  at  $20^\circ$  for the particular crystal used was  $74^\circ 54' 52''$ , while at  $-180^\circ$  it had become reduced to  $74^\circ 40' 36''$ .

In the case of **quartz** the rhombohedron angle  $(100) : (\bar{1}22)$  or  $(10\bar{1}1) : (\bar{1}011)$  was  $103^\circ 33' 36''$  at  $+21^\circ$ , and had increased to  $103^\circ 36' 12''$  at  $-166^\circ$ .

For all three substances the change of angle per degree of temperature decreased as the temperature fell.

These experiments form the natural corollary to the higher temperature ones of Wright, and show that between the lowest and highest temperatures attained,  $-180^\circ$  to  $+600^\circ$  C., the cleavage rhombohedron angle  $rr$  of calcite alters to the extent of one degree and a quarter, and the over-pole rhombohedron angle  $rr'$  of quartz by  $24'$ , between  $-166^\circ$  and  $+575^\circ$  C. Together the results give us a remarkably complete temperature history of these two important minerals.

Incidentally, Goldschmidt mentions a beautiful experiment met with during the investigation, concerning the crystallisation of carbon bisulphide  $\text{CS}_2$  at the temperature of liquid air. If a little iodine be first dissolved in the liquid  $\text{CS}_2$ , it is taken up into solid solution during the crystallisation of the carbon bisulphide, and renders the doubly refractive acicular crystals pleochroic; they appear carmine red in light vibrating parallel to the length of the needles, but quite colourless in light vibrating perpendicularly to the prism length.



## CHAPTER XXVII

### TWO AND THREE CIRCLE GONIOMETERS, AND USE THEREWITH OF THE GNOMONIC PROJECTION

THE goniometer No. 2*a* of Fuess and the similar Troughton and Simms instrument, described in Chapter III., are the best types of ordinary single-circle goniometers. They have been shown to be fully adequate for all the purposes of crystal measurement to single minutes of arc at the ordinary temperature, while the larger single-circle goniometer No. 1*a* of Fuess, described in the last chapter, is equally the best instrument yet constructed for similar measurements to seconds of arc at either the ordinary or higher temperatures, and is usually reserved (as regards crystal-angle measurement) for the higher temperature work, as the No. 2*a* is handier and its reading to half-minutes is all that is ever necessary for ordinary-temperature work. With their aid every zone on the crystal can be measured through the whole  $360^\circ$ , and the measurements may be repeated without a break if desired, in order to verify that the readings are the same and that there has consequently been no movement of the crystal on its wax setting on the crystal holder. It is obviously necessary, however, from time to time, after the measurement of two or three or more adjacent zones, to re-set the crystal on the wax, in order to place a further number of zones conveniently for adjustment and measurement. The number of settings is not large, however, and can often be reduced to four or five at most when the general plan of the crystal is known, as is the case during the measurement of all the crystals after the first, of the ten usually measured of a new substance. When full use is made of the range of motion of the segmental adjusting movements, a crystal possessing numerous zones may often be completely measured with three settings. For the purposes of the most refined measurement, in the case of original investigation, the necessity for a few settings is as nothing compared with the accuracy, rigidity, and simplicity of such a goniometer, and particularly with the advantage of being able to complete the whole  $360^\circ$  of each zone, and thus to verify the absence of slipping on the part of the crystal by proving that the first and last readings, for the same face originally started with, are identical. Lastly, the single-circle goniometer pre-eminently emphasises the occurrence of crystal faces in zones, and lends itself admirably to the determination of the zonal

relationships and of the indices of the crystal faces, thus bringing home to the mind the law of rational indices in an unmistakable manner.

While these considerations render the single-circle goniometer the basis of all sound knowledge of the symmetry of crystals, there have of recent years been coming into use two- and three-circle goniometers. They have chiefly been employed by their inventors for work of an intermediate character between student work and the highest kind of research, such for instance as the rapid investigation of unknown substances by Fedorov's new method of crystallochemical analysis (see Chapter XXXIV.), or of new specimens of known crystallised minerals, many of which crystals are only developed at one end of a prism zone, having been attached to a cavity wall at the other end, but are very rich in faces at the end which is developed. The completion of the zones other than the prism zone will here be a matter of no consequence, as only half a zone will be present, and all these half-zones will be able to be measured with a three-circle goniometer with a single setting, and the single complete zone can also be completely measured on one of the circles. Moreover, three-circle goniometers have been employed for the experimental solution of all the unknown elements of the numerous spherical triangles on a stereographic projection. Hence it is essential that a description of the best forms of these instruments should be given. It has been left to the conclusion of the goniometrical part of this book in order to emphasise the fact that the single-circle goniometer described in Chapter III. and referred to throughout is the only essential form, and that these multiple-circle goniometers may well be left until considerable experience with crystal measurement has been acquired; also, that if expense of equipment be a consideration of moment, they may be disregarded, an excellent single-circle instrument being fully adequate for all the purposes of either teaching or research.

It is interesting that the British father of our science, Miller, so long ago as 1874, constructed a two-circle goniometer, by arranging a vertical-circle goniometer on the top of an ordinary horizontal-circle instrument, and an account of it and the work done with it has been published by his successor in the Cambridge chair of Mineralogy, Professor Lewis.<sup>1</sup> In 1889 Fedorov gave a description of a two-circle goniometer<sup>2</sup> similar to that of Miller, but instead of the separate collimator and telescope an auto-collimating telescope was used, that is, one in which the same optical tube was made to serve for both purposes, with the aid of a reflecting prism only half closing the aperture at the common focus of the objective and eyepiece. This, however, has been found to be a disadvantage, as the images from small faces are faint owing to the perpendicular incidence of the light on the crystal face. In 1893 V. Goldschmidt<sup>3</sup> quite independently described another similar two-circle goniometer, but in which the ordinary collimator and telescope were used, and in the same year Czapski<sup>4</sup> published his account of the now well-known instrument

<sup>1</sup> *Zeitschrift für Krystallographie*, 1883, 7, 619.

<sup>2</sup> *Proc. Min. Soc.*, St. Petersburg, 26, 458.

<sup>3</sup> *Zeitschr. für Kryst.*, 1893, 21, 210.

<sup>4</sup> *Ibid.*, 1893, 21, 574.

which bears his name, and which, in the form now constructed by Fuess, will next be described, together with the mode of using it. Five years later Professor V. Goldschmidt,<sup>1</sup> who has made two-circle goniometry a speciality at Heidelberg, described a greatly improved form of his two-circle goniometer, and an account of it and of his method of employing it will afterwards be given. A much more recent (1914) form of the instrument, similar in principle but differing in details, employed by Fedorov in his crystallochemical analysis, will also be described and illustrated. Finally, a new model of the V. Goldschmidt two-circle goniometer has been elaborated, and constructed at Heidelberg in the year 1920, with numerous improvements suggested by long experience; an account and figure of this instrument, probably the best two-circle goniometer yet constructed, will be given at the conclusion of the section on the V. Goldschmidt instrument.

**Principle of Two-circle Goniometry.**—The crystal is adjusted on such a two-circle goniometer (one circle being horizontal and the other vertical) so that a face of importance with respect to the symmetry is parallel to the circle carrying the crystal on its axis of rotation. This face is termed the pole-face. The position of any other face is accurately given by its two co-ordinates, one of which, the azimuth  $\phi$ , is read off on the same circle carrying the crystal, and the other of which, the polar distance  $\rho$ , is afforded by the second circle. The azimuth corresponds to longitude, and the polar distance to latitude. The zonal relationships are not directly shown by these co-ordinates, but from the latter it is possible with some considerable trouble to calculate the crystal elements and the facial indices; the formulæ employed by Fedorov and Goldschmidt, however, are complicated and do not lend themselves to the simple methods of logarithmic calculation which have been shown in the earlier part of this book to be so useful and convenient. A concise account of Goldschmidt's method will, however, be given, following the description of his instrument, and in describing the use of the gnomonic projection.

**Czapski Theodolite Goniometer.**—This instrument, as improved by Leiss, Wulff, and Stöckl, and constructed by Fuess, is shown in Fig. 365 on the scale of one-quarter the real size.

The horizontal circle  $a$  is carried on an axial cone rotating within a fixed cone  $b$  supported by a tripod  $c$  of the usual character in the Fuess goniometers, except that one limb is longer than the other two in order to afford room for the bearing pillars  $d$  of the vertical circle  $e$ . The horizontal circle is divided on silver directly to  $20'$  and reads with the aid of the usual pair of verniers to minutes of arc. It is rotated by the capstan wheel  $f$  from below, by means of the five handles. The crystal  $g$  and its adjusting segments  $h$  and centring movements  $i$  are carried as in the ordinary No. 2a goniometer, at the head of an innermost axis of steel  $j$ , bearing a screw thread on its lower portion, and lying within and keyed to another axis rotatable within the circle axis; the steel axis is thus capable of being raised or lowered without rotation, by means of the milled-headed nut near its lower end. The adjusting movements are capable of fixation to the steel axis by the screw  $k$ . The circle may be clamped to the tripod by the screw  $l$ , and finely adjusted by the other screw  $m$  at right angles, which presses against an upright projection carried by an arm underneath the circle, a spring piston pressing the projection against the adjusting screw on the other side.

<sup>1</sup> *Zeitschr. für Kryst.*, 1898, 29, 333.



The axis of the vertical circle is carried by the upright support *d* which terminates in the axial bearing cone *n*. The telescope *o* and collimator *p* are also carried about this same axis in theodolite fashion. The circle is rotated by a large conically-shaped capstan head *q* fitted with five manipulating handles; it is read by two microscopes *r*, and affords, with the aid of the two corresponding verniers *s*, readings to minutes of arc, the circle itself being directly divided to 20' as in the case of the horizontal circle. This vertical circle is capable of being fixed to the bearing by the screw *t*, and of being finely adjusted by another screw *u*. The axle bearing is hollow to admit of the crystal being viewed through a lens carried near the inner end of the boring, a small diaphragm *v* being placed at the other and outer end. The crystal may thus be observed and set to the intersection of the two axes of the two circles. The telescope

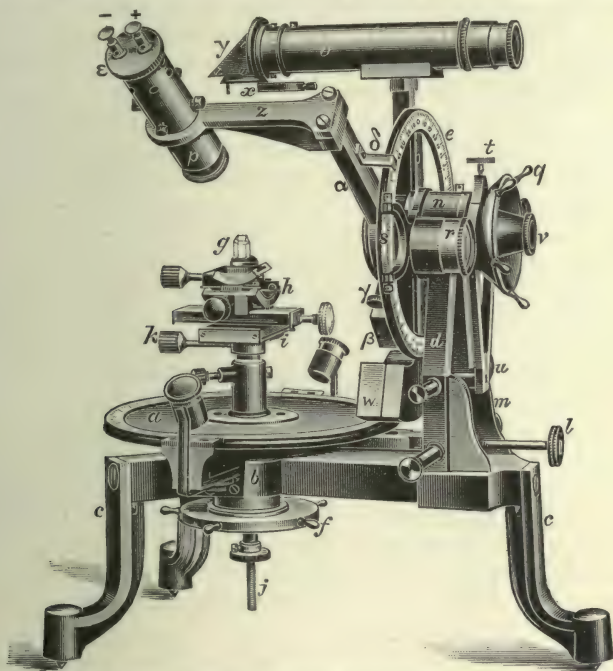


FIG. 365.—Czapski Two-circle Theodolite Goniometer.

o is carried by a radial arm continued into a counterpoise *w*, and is provided with the usual viewing lens *x* at the objective end, a totally reflecting prism *y* between the two lenses directing the rays from the crystal into the telescope. The collimator *p* is carried on the elbow *z* of another radial arm *a*, the boss of which rotates round the fixed bearing outside the telescope boss, and which is also continued into a counterpoise  $\beta$ . The collimator can be arranged at any angle to the telescope and clamped there by means of the fixing screw  $\gamma$ ; the angle is read off on the circle with the aid of the index  $\delta$ . The collimator carries at its outer end a little tubular fitting  $\epsilon$  in which is contained a 4-volt glow-lamp, or else an alternative one carrying an adjustable mirror, either fitting also containing a condensing lens for the illumination of the signal, the Schrauf cross-signal being employed. When the mirror is used, it is arranged to reflect the light from an ordinary electric glow-lamp placed a yard or two distant along a prolongation of the horizontal axis of the vertical circle *e*, so that for all positions of the collimator the light is reflected along the axis; a little circular

opaque screen is used to ward off the central part of the light (not required by the mirror) from the crystal. An iris diaphragm may also be fitted in front of either the collimator or telescope, for the purpose of isolating the light reflected from any one part of a crystal face, the viewing lens being placed in position against the telescope objective in order to observe the crystal, so that the observer can see when he has properly screened off with the iris diaphragm the light from those parts of the face which are not desired to afford an image of the signal. On removing the viewing lens the image from the required portion of the crystal face will be seen. This renders the goniometer well suited for the study of vicinal faces, discussed in Chapter XXIV.

This goniometer enables all the faces of the upper half of the crystal to be adjusted, and also those for  $30^\circ$  below the equator.

**Method of use of Czapski Theodolite Goniometer.**—The crystal is observed through the microscope within the boring of the axle of the vertical circle, from  $v$ , and a prominent zone of faces is adjusted. The telescope  $o$  is then rotated down about  $20^\circ$  below the equator (that is, till its arm which is vertical in Fig. 365 is inclined downwards  $20^\circ$  below the horizontal). When the arm is horizontal the circle readings (those for the equator) are  $90^\circ$  and  $270^\circ$ . The collimator  $p$  is then arranged at the same angle upwards from the equator on the same side, so that the vertically adjusted zone of faces of the crystal will afford a series of reflected images of the signal in the field of the telescope as the crystal axis is rotated. The adjustment is then perfected so that all the images pass at the same height in the field of the telescope. This only occurs when the normals to the faces are all precisely in the horizontal plane, that is, in the plane perpendicular to the vertical axis of the instrument. The collimator is then to be raised or lowered slightly until the images pass through the centre of the field of the telescope, when the two optical tubes will make the same angle with the horizontal plane. They should then be fixed in this position and retained so during the whole series of measurements. The positions of the poles of all the faces in the zone should then be read off on the horizontal circle  $a$ . The reflections of all other faces will be found by simultaneous rotation of both circles  $e$  and  $a$  (the former with the telescope and collimator remaining clamped to it in the fixed positions), and they should be finely adjusted and their positions on the two circles read off. The reading on the horizontal circle  $a$  gives the azimuth co-ordinate  $\phi$ , and that on the vertical circle  $e$  gives the other co-ordinate, the polar distance  $\rho$ . The determination is much easier when there is a face developed perpendicular to the zone of adjusted faces; this is recognised by its image remaining fixed when the crystal and the vertical axis carrying it are rotated. The positions (polar distances  $\rho$ ) of all faces lying in a zone with this "pole-face" and with one of the vertically adjusted faces are then easily determined by rotation of the horizontal axis and reading of the vertical circle  $e$  alone, as their azimuth  $\phi$  (reading on horizontal circle  $a$ ) is the same as that of the vertical face.

The poles of the adjusted faces are drawn on the primitive circle of the stereographic projection, and the other measurements are subsequently also graphically expressed on the projection in the usual manner.

**V. Goldschmidt's Two-circle Goniometer.**—The essential difference

between this instrument, constructed at Heidelberg by P. Stoë, and which is illustrated in Fig. 366, and that of Czapski is that the crystal is borne by the vertical circle V instead of by the horizontal circle H. Moreover, the telescope and collimator are arranged horizontally, and do not travel with either circle.

Both circles are divided directly into quarter-degrees, and read by means of their verniers, with the aid of two low-power microscopes, to half a minute of arc. The conical axis of the horizontal circle, which is rotatable in the rigid central hollow cone of the tripod, carries in a central boring a narrow column, tapped below, and capable of being raised or lowered by means of the driving nut *a*, and terminating in a

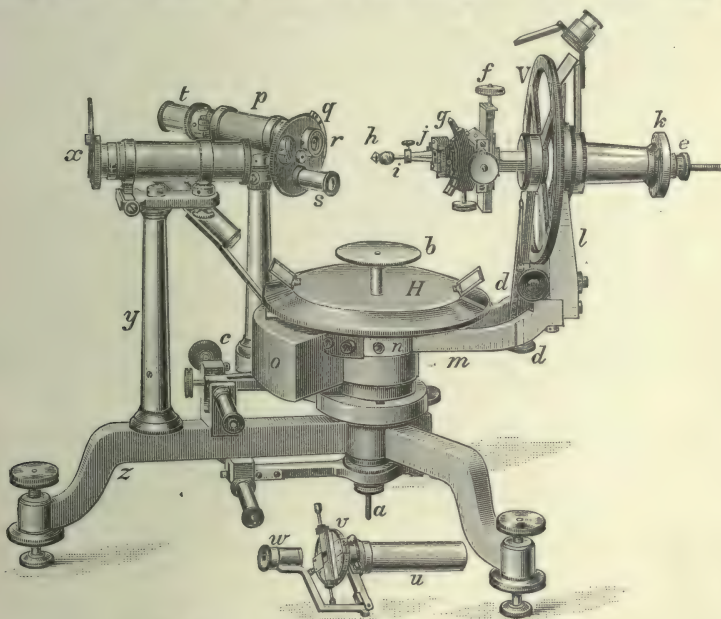


FIG. 366.—V. Goldschmidt's Two-circle Goniometer.

little disc *b*, which serves as a tabular stand for a glass cell or prism containing an immersion or highly refracting liquid, which may occasionally be required. A fine adjustment is provided for each circle, that for the horizontal circle being marked *c* and that for the vertical circle *d*. The axis of the vertical circle also has a central boring in which a triangular prismatic rod is capable of sliding, being driven in the direction of its length (horizontally) by the mother-nut *e*; this prismatic slider carries the centring movements *f* and the adjusting segments *g*, the second segment, as usual, carrying the crystal *h*, fixed on its holder *i* by goniometer wax. This crystal holder *i* is capable of rotation and about two centimetres of sliding, in its bored support *j* carried by the second segment, thus enabling some preliminary adjustment of the crystal to be effected.

The vertical circle V is rotatable by means of the milled flange *k*, and is carried by the vertical arm *l* of the elbow-piece *m* radiating from the massive ring *n*, which fits around the conical column of the horizontal circle H and carries the latter with it; a counterpoise *o* for the weight of the vertical circle and its carrying arm is provided on the other side of the ring. The vertical supporting arm *l* for the circle V is



adjustable by the small screws seen at its junction with the elbow-piece *m*, so as to afford the means of adjusting the plane of the vertical circle exactly at right angles to that of the horizontal circle. The ring *n* is made slightly excentric in order to afford further possibility of adjustment of this nature.

The telescope *p* carries in front of the objective a revolving disc *q* provided with three openings: one is vacant, another *r* contains a lens furnished with four centring screws, and the third *s* contains a higher power at the end of a short tube to bring it closer to the crystal. Two eyepieces *t* and *u* are provided, the lower power *u*, shown separately at the base of the illustration, being fitted with a variable rectangular diaphragm *v*, for the suitable restriction of the field. The combination of *r* with *t* enables the telescope to afford an enlarged image of the crystal, suitable for the centring and observation of the smaller crystals employed, or of the details of portions of the larger crystals. When the vacant aperture and the higher power eyepiece *t* are combined, an enlarged image of the goniometer signal is given. If the front lens of *t* be withdrawn a small image of the crystal without the image of the cross-wires is afforded, in a large field. This serves for coarse adjustment, and even for many measurements. It is convenient, as it gives a complete view of the crystal, even when the latter is large. The lens *s* with the low-power eyepiece *u*, including its front lens *w* supported by the bracket, affords a strongly magnified image of a very small crystal. The low power *s*, with *u* pushed further in, combined with the lens *r*, gives a somewhat larger field of view and a less magnified image than the last-named combination. The combination of *s* with the low-power eyepiece *u*, but without the front lens of the latter, affords a diminished reflection of the signal, of greater intensity.

The collimator *x* is carried on an adjustable table at the head of the vertical column *y*, which rises direct from the massive basal tripod *z*. The form of signal used is that of a cross, the usual provision for the adjustment of which is afforded, both as regards its position in its own plane and with respect to accurate focussing without parallax.

Very full directions for the adjustment of the instrument are given in the 1898 memoir (*loc. cit.*). As the crystal is borne by the axis carried

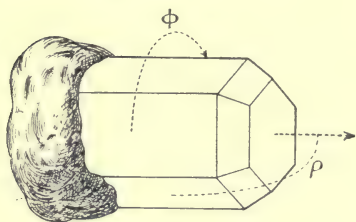


Fig. 366a.—Arrangement of Crystal, showing the Angular Co-ordinates.

by the vertical circle V, it is usually arranged with the prismatic zone of faces horizontal and with the basal plane "pole-face" vertical (or thereabouts if the crystal be monoclinic or triclinic), as shown in Fig. 366a.

In order to render it quite clear which angle is considered as azimuth  $\phi$ , and which as the polar distance  $\rho$ , these angular co-ordinates are indicated in the figure by the dotted curves, and

labelled. In accordance with the statement on page 450, it will be observed that the azimuth is the angle read off on the circle which carries the crystal; in the case of this Goldschmidt instrument, therefore, it is read off on the vertical circle, while in the case of the Czapski instrument (Fig. 365) it is the horizontal circle which affords  $\phi$ .

The new 1920 model of the V. Goldschmidt two-circle goniometer, to which allusion was made on page 450 as being probably the best two-circle goniometer yet constructed, is shown in Fig. 367. It is constructed at Heidelberg by F. Rheinheimer, the successor of P. Stoë. One of these instruments has been supplied to Miss Mary W. Porter, Lady Carlisle

Research Fellow of Somerville College, Oxford, who has kindly permitted this illustration and description to be prepared. The chief improvements on the instrument illustrated in Fig. 366 are as follows: The mode of construction of the axes and their vertical and horizontal bearings and supports enables the horizontal circle to be rotated to any extent with respect to the vertical circle carrier, so that any pole-position can be employed, and the observer is not limited to particular and possibly very inconvenient pole-positions. Also, by mounting the vertical circle support on a slider, provided with rapid and fine motions along a horizontal arm carrying a scale, much greater latitude is afforded as regards the size of crystal investigated, and a greater extent and freedom of movement and possibility of fine

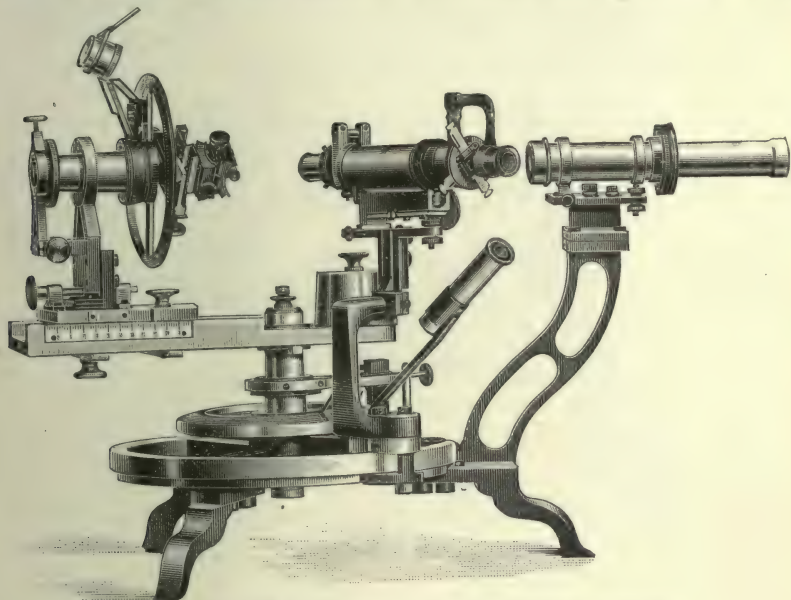


FIG. 367.—New 1920 Model of V. Goldschmidt Two-circle Goniometer.

adjustment to a desirable position<sup>1</sup> is afforded to the vertical circle. The optical arrangements are also improved by the provision of a telescope affording a considerably larger field, by the addition of a condenser to the collimator and of an iris diaphragm to the telescope for hand adjustment, and by the rearrangement of the accessory lenses in a more convenient manner conducive to rapid interchange.

**Fedorov's Two-circle Goniometer.**—The latest (1914) form of two-circle goniometer employed by Fedorov<sup>1</sup> in his great work on crystallochemical analysis is shown in Fig. 368.

<sup>1</sup> *Zeitschr. für Kryst.*, 1914, 54, 24.

It was with the deepest regret that his British friends and co-workers in crystallography learnt early in the year 1920 of the untimely death of Prof. Fedorov during the troubles in Russia. His published work on this subject, so frequently referred to in this book, forms an imperishable memorial of a master mind and of an industry truly remarkable.

In this instrument, constructed by Fuess, a signal separate from the instrument is provided, at some considerable distance away. Fedorov considered that this method affords better illuminated images of the signal from the poorer faces of the more or less imperfect crystals which alone are often obtainable, or to hand, for the purposes of crystallochemical analysis. The instrument consists essentially of two parts—a fixed part and a movable one. The fixed portion is formed by the telescope, the only optical tube, and its rigid tripod stand, which also carries the rigid outer cone in which the axis of the horizontal circle revolves. The movable portion consists of the two circles and the supports of the vertical circle. The telescope is directed towards the geometrical centre of the instrument, while the movable portion is rotatable around the vertical axis which contains that geometrical centre.

The rotation angle (the polar distance  $\rho$ ) is read on the horizontal circle with the aid of two verniers and reading lenses; the verniers are independently rotatable,

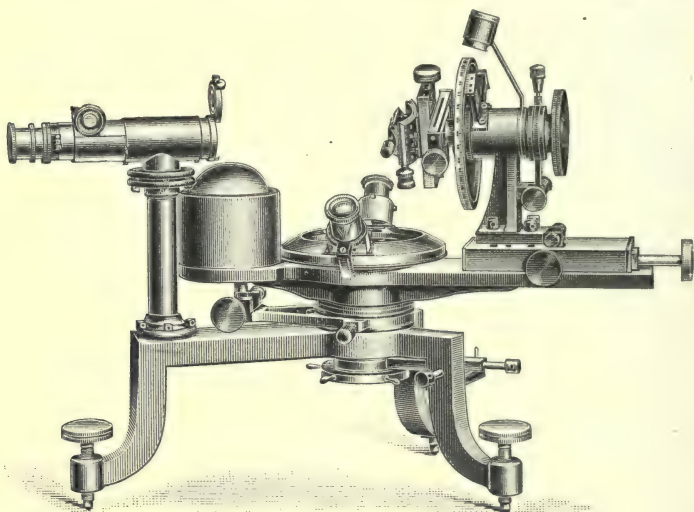


FIG. 368.—Fedorov's Two-circle Goniometer.

so that the zero point of either can be brought to any desired reading of the circle. The mobile vertical circle, on which the azimuth  $\phi$  is read, and the bearings of its horizontal axis, are carried on a column borne by a large slider, moving along a horizontal arm, which is pivoted round the main vertical axis of the goniometer; the arm is continued on the other side of the main central axis, where it carries a carefully adjusted counterpoise, which forms a conveniently grasped object wherewith to effect the rotation of the arm and all that it carries, by the hand. The horizontal circle may either be clamped to the arm, so that the vertical circle and its support move with it, as during the measurement of  $\rho$ , or it may be rotated alone, by the capstan wheel below the axis. The horizontal axis of the mobile vertical circle also passes through the geometrical centre of the instrument.

The details of the instrument will be clear from the illustration Fig. 368, the various fine adjustments being obviously of the usual character provided in the Fuess instruments; the telescope, and the centring and adjusting movements carried by the mobile vertical circle, are also of the well-known character generally supplied by Fuess and already described in connection with the No. 2a goniometer.

The main novelty of this Fedorov instrument as compared with that of Goldschmidt



is the use of a separate and distant signal. A window-slit illuminated by daylight, or a table slit (a Websky slit or a cross-slit) illuminated by a powerful lamp and focussed by a collimating lens as described on page 47, would serve the purpose. For two-circle goniometry a cross-slit is usually the most convenient form of signal.

**Essentials of the Method of Two-circle Goniometry.**—The main principle of two-circle goniometry is that every face of the crystal under investigation has its position defined with reference to a pole, and to a direction which is assumed as first meridian. The basal plane, in crystals belonging to the systems with rectangular axes, is naturally and preferably chosen as the pole-face, and the great circle passing through the pole of this face and the pole of the primary pinakoid face (010) is the most suitable as first meridian. Even in the monoclinic and triclinic systems the plane perpendicular to the primary prismatic zone containing (100) and (010), supposing such a zone to be developed, is best taken as the pole-plane. It will be clear from Fig. 366*a* that the angle between the normal to the pole-face (the basal plane (001) in the figure) and the normal to the face the position of which is to be defined is the polar distance  $\rho$ , as measured on the horizontal circle H of the V. Goldschmidt or Fedorov goniometer; both faces are adjusted perpendicular to H, and the signal images reflected from each in turn brought to the cross spider-lines, as in ordinary crystal measurement. Also that the angle between the normal to the first meridional pinakoid face, (010) in the case before us, and the normal to another possible prism face, in the same zone (another meridional great circle) with the pole-face and the face to be defined, is the azimuth  $\phi$ , as measured on the vertical circle V (carrying the crystal) of the Goldschmidt or Fedorov instrument. These two angular co-ordinates,  $\phi$  and  $\rho$ , are thus measured directly when the pole-face is developed as a crystal face. We start with the pole-face and first-meridian face adjusted perpendicular to H, and the former reflecting the signal-image to the cross spider-lines. By rotation of V for the angle  $\phi$  any other third face can be brought perpendicular to H, the pole-face remaining also adjusted. Then by rotation of H for the angle  $\rho$  the other third face can also be brought to reflect the signal-image to the spider-lines. It will thus be clear that the  $\rho$  readings on H give the positions of facial poles along diametral zones of the stereographic projection, of which the reference pole forms the centre; and that these zones are adjusted one after another by rotation of V, until each edge in turn of the pole-face is brought vertical, the  $\phi$  readings on V for such adjustments affording the positions of the facial poles along the primitive circle of the projection. The angles for the three mutually rectangular pinakoids (001), (010), and (100) would be:

	$\phi$	$\rho$	
(001)	0° 0'	0° 0'	of the signal when the face is brought exactly normal to the line bisecting the angle between the optical axes of the telescope and collimator, and this zero position of exact normality, the reference direction, has first to be fixed and determined, its angular position, as given on the horizontal circle of the V. Goldschmidt or Fedorov goniometer, being designated by Goldschmidt $h_0$ . To effect its determination, the telescope and collimator are first clamped at the convenient mutual angle apart. Then a well-reflecting truly plane
(010)	0 0	90 0	
(100)	90 0	90 0	

Now a face on the crystal affords the reflections

surface, a truly worked glass plate being provided for the purpose (Fedorov uses the flat surface of a glass hemisphere), is mounted and centred approximately parallel to the vertical circle (V. Goldschmidt or Fedorov instrument). It is then adjusted so as to bring the signal reflection to the cross spider-lines, by suitable rotation of the two circles, and the reading on the horizontal circle is recorded as  $h_1$ . The other circle is then rotated  $180^\circ$ , the signal-image again adjusted by use of the crystal-adjusting segments, and the reading again taken on the horizontal circle and recorded as  $h_2$ . Then the desired normal position of reference  $h_0$  is:  $h_0 = \frac{1}{2}(h_1 + h_2)$ .

By repetition and closer approximations it can eventually be arranged that the signal-image remains immovable at the intersection of the spider-lines during a revolution of the crystal-carrying circle (V in the Goldschmidt or Fedorov instrument). This final position is actually  $h_0$ .

The crystal is then mounted instead of the glass-plate reflector, with the prismatic zone approximately parallel to the axis of the circle carrying it (V in the V. Goldschmidt or Fedorov instrument); this prismatic zone is then accurately adjusted parallel to the circle axis, with the aid of the adjusting segments. The other (horizontal) circle is then clamped at  $90^\circ + h_0$ . Each of the prism faces in turn can then be brought, by rotation of the crystal-carrying circle, so that the reflections of the signal one after another pass across the field in the line of the vertical spider-line, and each in turn can be adjusted to the cross-spider-line centre. If the crystal has a basal plane face (001) at right angles to this prism zone, that is, if it has the polar reference surface actually developed as a face, this face would afford the signal reflection at  $h_0$  itself, being  $90^\circ$  from each prism face. The reading on the crystal-carrying circle (V) for the face (010) of the prism zone just adjusted and measured is, of course, the reference first-meridional reading  $v_0$  for this circle. As it depends on the position of attachment of the crystal, this zero value  $v_0$  differs for every different crystal attached or for every different attachment of the same crystal (if more than one be necessary).

The adjustments being thus completed, and the zero readings  $h_0$  and  $v_0$  for the two circles thus determined, the position of any face other than (001) and (010), and of (001) itself if the crystal be monoclinic or triclinic, can be ascertained by causing the signal-image to be reflected from it by suitable rotation of the two circles, adjusting the image to the cross-wire centre, and taking the two readings corresponding on the two circles. Supposing the V. Goldschmidt or Fedorov instrument to be employed, the reading on the vertical circle V, which may be termed  $v$ , and that on the horizontal circle H, which may be designated  $h$ , at once afford the two position co-ordinates  $\phi$  and  $\rho$  by taking the difference from the zero positions  $v_0$  and  $h_0$ , that is:

the azimuth  $\phi = v - v_0$ , and the polar distance  $\rho = h - h_0$ .

This is done for each face in turn, first for the faces of the prismatic zone, and then subsequently for every face of every zone which it is desired to investigate and measure on the crystal.



**Herbert Smith Three-circle Goniometer.**—In order to render the theodolite method free from the grave disadvantage of ignoring zonal relationships and the law of rational indices, an additional circle was added by Herbert Smith, which enables the crystal to be adjusted once for all, and at the same time both the angles between the faces of any one zone and the position of this zone on the crystal, with reference to other zones and the general symmetry, to be determined by direct measurement. The first form<sup>1</sup> was simply obtained by adding to an ordinary No. 2a Fuess goniometer a second circle arranged vertically, which carried by means of a rectangular elbow bracket-bearing a third circle supporting the crystal at the end of its axis, with the usual adjusting and centring movements. With this adapted instrument, however, measurements can only be made through little more than a right angle in any particular zone other than the zone of reference, without readjustment of the vertical and third circles. In a second instrument,<sup>2</sup> which was constructed by Messrs. Troughton and Simms, this difficulty is largely overcome by reflecting the line of reference—which is the line bisecting the angle between the telescope and collimator in the ordinary single-circle goniometer and the adapted one just referred to—at right angles to its normal position by means of mirrors, so that on rotation of the vertical circle round the axis of the horizontal circle the axis of the vertical circle may be brought into coincidence with the line of reference in two positions on diametrically opposite sides of the centre, and still be free for somewhat further movement beyond the 180° of movement thus already afforded. Both these instruments will now be briefly described, for, in spite of the advantage of the second form just referred to, the adapted Fuess instrument is very handy in actual practice and has been found extremely useful.

The essential principle is the same in both instruments. There are three circles arranged as follows :

A. The horizontal circle, the axis of which is vertical and fixed in space, permitting only rotation of the circle about it; the axis is also perpendicular to the line of reference of the telescope and collimator.

B. The vertical circle, the axis of which is horizontal and at right angles to that of A, but is movable in the horizontal plane.

C. The third circle, the axis of which may be brought to occupy any desired direction in space and therefore also with respect to the axis of A, but which is always at right angles to that of B.

All three axes and the line of reference (the normal to the crystal face when adjusted so that the signal-image is symmetrical to the telescope spider-lines) intersect in the optical centre of the instrument.

Fig. 369 shows the instrument obtained by the addition of a two-circle arrangement constructed by Troughton and Simms to a No. 2a Fuess goniometer, in which it replaces the crystal-holding axis. A is the horizontal circle of the original Fuess instrument, and B and C are the two new circles. The latter are carried by a rigid horizontal plate *a*, which may either be firmly attached to the horizontal circle A, or may be rotated independently of the latter, the plate having an axial cone below it capable of rotating in the conical axial boring of A. The elongated plate carries

<sup>1</sup> *Mineralogical Magazine*, 1899, 12, 175.

<sup>2</sup> *Ibid.*, 1904, 14, 1.



at opposite ends respectively the upright supports *b* for the cone *c* in which the vertical circle *B* rotates, and a counterpoise *d* for the same and all that it carries, including the third circle *C*. The holes for the screws by which the column is attached to the plate are slotted, in order to provide means of accurate adjustment of the two extra circles to the optical centre of the instrument. The third circle is of aluminium, in order to reduce the overhanging weight to a minimum; and it is fitted to the vertical circle by means of a similar plate and adjustable elbow-bearing *e* in the

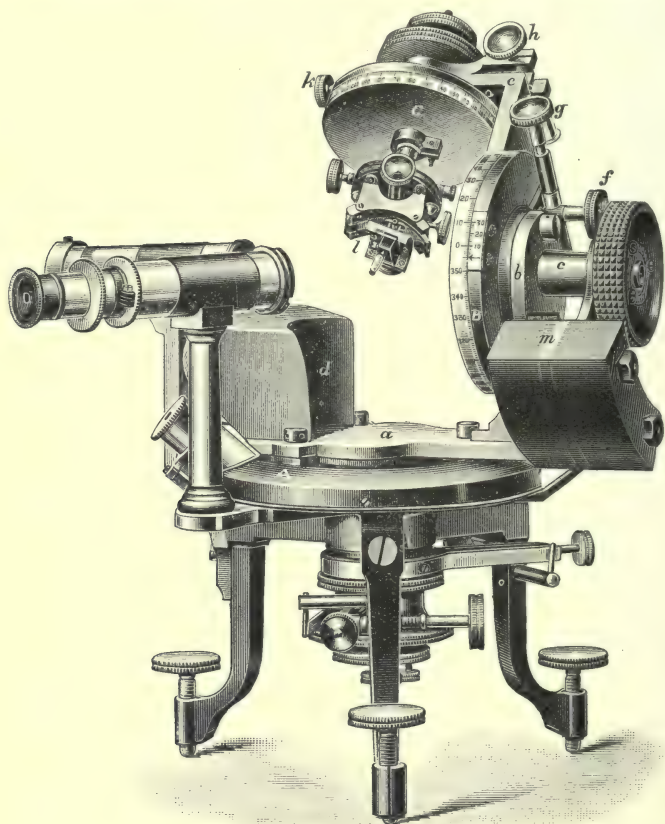


FIG. 369.—First Form of Herbert Smith Three-circle Goniometer.

manner which will be clear from Fig. 369. The axis of the circle *C* has also three adjustment screws, two to bring it into a plane parallel to the vertical circle *B* and one to make it intersect the axis of this circle. Both circles have clamps *f* and *k* and slow-motion screws *g* and *h*, and fixed verniers reading to minutes. The crystal-holder *l* is carried by the third circle *C*, and the latter is counterpoised by a weight *m* at the outer end of the bearing of the vertical circle *B*.

These arrangements render it easy for the reading on the circle *A* to be made  $0^{\circ} 0'$  for a crystal face parallel to the vertical circle *B*, and the graduations of this circle are so arranged that when the axis of

circle C is vertical the reading on B is also  $0^{\circ} 0'$ . The circles C and B are about 9 and 11 cm. in diameter respectively, which permits of the vertical circle B being turned about the axis of the horizontal circle A for about  $190^{\circ}$ , when the telescope and collimator are inclined to one another at  $70^{\circ}$ ; the circle C may be turned about the axis of circle B through about  $240^{\circ}$ , when that axis bisects the interior angle between telescope and collimator.

In using the instrument, a zone of faces, preferably the zone of greatest symmetry if it be known, is adjusted parallel to the axis of circle C. As this circle is rotated the various faces in the zone are in turn brought parallel to circle B, and if the circle A be rotated until it reads  $0^{\circ} 0'$  the image from a face parallel to B will be visible adjusted to the spider-lines. The axis of circle C should also be arranged vertically by suitable rotation of circle B. The faces of the adjusted zone may then be measured on circle C, as the circle is rotated and each face in turn comes parallel to circle B and affords an adjusted image in the telescope. If, then, circle C be clamped when some face is thus adjusted, and circle B be rotated, any zone containing this face may be brought parallel to the axis of the horizontal circle A and measured on that circle. It thus amounts to being able to make two-circle measurements with any face of the crystal as reference face, instead of being confined to one pole-face (with any one setting), as is the case with a two-circle goniometer. Any zone may be adjusted by means of the circles B and C so as to be parallel to the horizontal circle A, and can thus be measured on the latter circle. Hence circle A gives the angles in the zone, and circle B gives the angle between this zone and the reference zone.

Fig. 370 shows the later instrument of Herbert Smith, in which a much greater angular range is obtained by the reflection of the line of reference, the telescope *a* and collimator *b* being very close together so as to be nearly parallel and pointing to one side of the centre. It is constructed by Troughton and Simms.

The tripod base *c* carries within its central cone *d* in the usual goniometrical manner the rotatable conical axis of the horizontal circle A. The scale on the bevelled edge of the circle-plate is divided to  $10'$ , and is read by a pair of micrometric microscopes *e* diametrically opposite to each other and carried by arms fixed to the tripod table; each micrometer head revolves once for every division of the scale and is divided into ten parts, each of which is subdivided into six, so that each of these smaller divisions corresponds to ten seconds of arc.

The second or vertical circle B is carried by an arm *f* attached to a thick plate *g* which is solid with the upper part of an inner stout conical axis rotating within the circle cone. The vertical circle B and all that moves with it can thus be rotated about the vertical axis of the whole instrument, quite independently of the horizontal circle A, and fixed anywhere with respect to it by means of a strong clamping screw. During this rotation the horizontal axis of the vertical circle thus moves radially with respect to the main goniometrical vertical axis (that of circle A) in the horizontal plane. The arm which carries the circle B is fixed to the cone-plate by four screws, which permit of its adjustment by other screws both towards the axis of circle A and at right angles to this direction. The circle B is read by a pair of micrometer microscopes *h* diametrically arranged on opposite sides of the divided limb, like those of circle A, and which read similarly to ten seconds. Two pairs of friction wheels are introduced between the main rotating parts, and a counterpoise *i* is provided

on the other side of the cone-plate to balance the weight of the vertical circle and all that it carries.

The third circle *C* is carried by a twice-bent arm *j* which, together with the axle cone *k* which rotates within that of the circle *B*, is worked out of a solid casting, and is also rigidly attached to the latter circle in such a position that the zero reading of the circle *B* is  $180^\circ$  or  $360^\circ$  in the two microscopes. The scale of the circle *C* reads

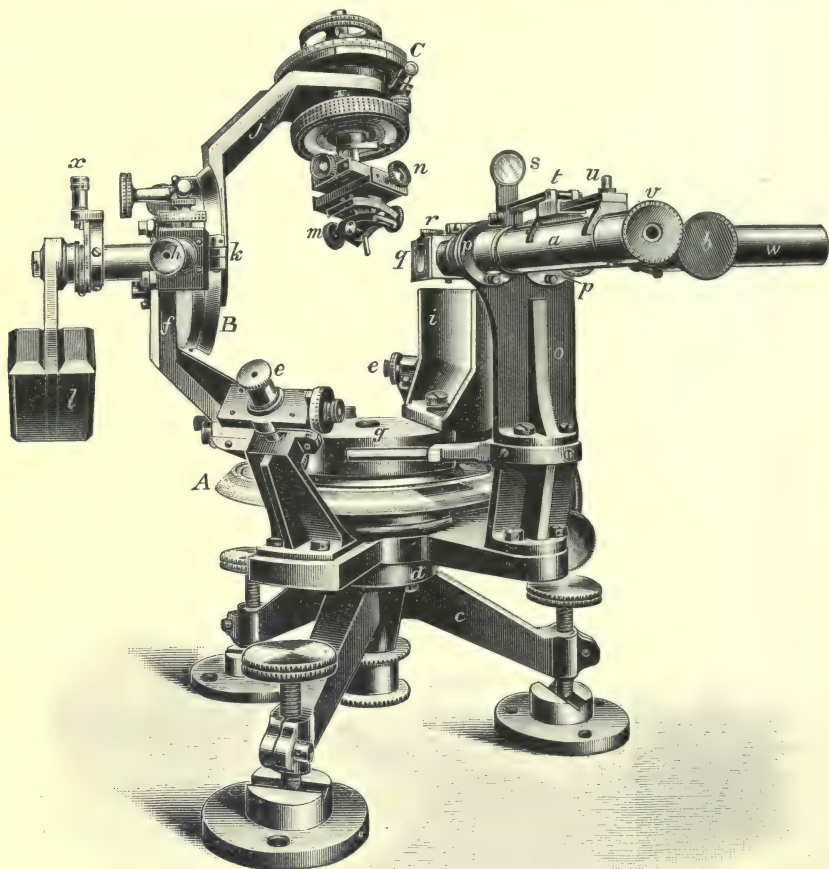


FIG. 370.—Later Form of Herbert Smith Three-circle Goniometer.

to minutes with the aid of a pair of verniers fixed to the axis in an adjustable manner by means of three pairs of adjusting screws. The counterpoise *l* for the third circle *C* is placed on the other side of the circle *B*, at the outer end of the axle.

All three circles are fitted with the usual Troughton and Simms clamping screw and screw-and-spring-piston fine adjustment movement. The crystal-holder and the adjusting segments *m* and mutually rectangular centring movements *n* are also of the usual kind, as described in Chapter III.

The telescope *a* and collimator *b* are separate optical tubes (not auto-collimating), but are supported by the same pillar *o* rigidly connected with the fixed tripod table.

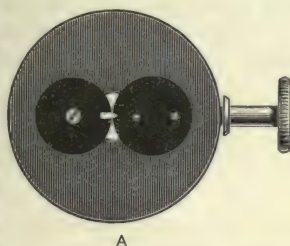


Each optical tube is carried within an outer tube, adjustable about a vertical axis and about a horizontal axis at right angles to the length of the tube, by means of three screws, *p*, working against strong spiral springs and passing through a flange into the fixed collar. The tubes may revolve about and be pushed along the direction of their length. A small reflecting prism is placed immediately outside the signal-slit of the collimator to permit of illumination from the side. At the inner ends of the optical tubes furthest from the observer they are provided with outer tubes *q* sliding over them like caps, each carrying an adjustable mirror of speculum metal and capable of fixation in the most desirable positions by means of split collars and tightening screws, the tubes and their mirrors being thus capable of either sliding or rotating. Each mirror is also capable of a further adjustment about a vertical hinge, by means of a screw working against a spring. The telescope mirror is placed further away than the collimator mirror, and its tube is cut away at the sides, so as to permit of the passage through it of the rays from the collimator mirror to the crystal, the reflected rays then passing back from the crystal face to the telescope mirror and thence through the telescope to the observer at the eyepiece. The speculum mirrors may be cleansed from any tarnish which develops by means of cotton-wool dipped in a mixture of two parts of absolute alcohol and one part of ammonia.

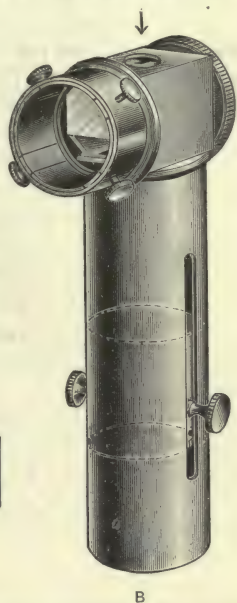
The viewing lens to be placed in front of the telescope objective is fitted on a horizontal hinge *r*, and occupies a recess on the top of the mirror tube when not in use, but can be placed in position, when it is desired to observe the crystal, by means of a lever arranged for the purpose outside the tube. Another lens *s* for placing in front of the eyepiece, to reduce the magnification when desirable, is carried on an arm *t* which is hinged on a slide movable along a bar *u* on the top of the telescope tube near the eyepiece *v*.

A special shape of collimator signal-slit is employed, which is shown at *A* in Fig. 371. The ordinary Websky signal is not sufficient, for the signal has to be adjusted to the horizontal as well as to the vertical spider-line of the telescope eyepiece. The illuminating light is sent down the side-tube *w*, and reflected into the slit by means of the small totally reflecting prism already referred to.

The mirrored axes of the telescope and collimator are inclined at about  $22^\circ$  to one another. The maximum possible rotation of the horizontal circle *A* is about  $240^\circ$ ; the axis of the vertical circle *B* can make with the line of reference angles of  $57^\circ$  towards the telescope and  $3^\circ$  towards the collimator. When *B* is near the collimator and its axis



A



B

FIG. 371.—*A*, Signal-slit of Three-circle Goniometer; *B*, Camera Lucida of Three-circle Goniometer.

coincides with the line of reference, the greatest rotation about its axis is  $188^\circ$ ; when *B* is on the other side it may be rotated for  $200^\circ$ .

To prevent excessive wear of the lower half of the fixed cone of the circle *B* two pairs of friction wheels are provided, one pair of which are near the counterpoise and are controlled by the spring balance *x*.

A further accessory of considerable use is a camera lucida, shown at *B* in Fig. 371. It consists of a double Amici prism, for reflecting the object in the direction of the

drawing-paper supported on the base-board of the instrument, and of a vertical tube in which lenses of various focal lengths, carried in an inner adjustable tube, may be inserted, to suit different scales of drawing or different distances of the eye. By this means also all parallax difficulties are eliminated. The horizontal upper shorter tube is provided with four screws by which the fitting may be attached to the eyepiece of the goniometer. It is particularly useful for the delineation of minute crystals. For the relative positions of faces on crystals with as small a cross section as 0.2 millimetre may be readily determined with the three-circle goniometer, but it is not so easy to sketch such small crystals in the ordinary way. If they are drawn by means of the ordinary camera-lucida attachment to a microscope there may be considerable uncertainty as to the identity of the faces; but when the crystal is on the goniometer any doubt is at once removed by an observation of the position of the face. It also proves very useful in the cases of faces which can only be determined by the position of the maximum light reflected from them, owing to distortion or curvature.

**Adjustment of the Three-circle Goniometer.**—A plate of parallel glass is mounted on the crystal-holder, and adjusted by the eye approximately parallel to the axis of circle A. The crossed spider-lines of the eyepiece are then illuminated by the Becker illuminator (Fig. 24) or by reflection from a glass plate employed in front of the eyepiece in a similar manner, and the image of the spider-lines is also caused to be reflected from the plate of parallel glass. The tube of the telescope mirror is next adjusted until the illuminated spider-lines and their images coincide. The plate is then rotated  $180^\circ$  and the image from its other surface similarly reviewed. If the horizontal spider-line and its image do not coincide, the plate must be adjusted through one-half the interval and the telescope mirror through the other half. The first surface is then reverted to, and if still not in adjustment corrected until it is; a few oscillatory observations and corrections may require to be made for the two surfaces before the agreement of the lines and their images is perfect for both.

The collimator mirror is next adjusted so that the signal-image, when brought into the centre of the field, is bisected by the horizontal spider-line. On rotation about the axis of the circle A, however, the centre of the image may not continue to traverse the horizontal line, showing that the mirrored spider-line is not perpendicular to this axis; if so, the tube of the telescope and also the mirror tube must be rotated through the same angle in the opposite sense until the adjustment is effected. If the image be not upright, a similar adjustment must be made for the collimator.

To adjust the axis of B perpendicular to that of A the parallel-glass plate is rotated about the axis of C until it is approximately perpendicular to that of B, and then C is clamped. By use of the crystal-adjusting movements the plate is adjusted so that the signal-image remains stationary on rotation of the plate about the axis of B. The latter is then adjusted with respect to A by the adjusting screws, until the image is exactly bisected by the horizontal spider-line. The axis of C is next adjusted perpendicular to that of B, by making it (the axis of C) coincide with that of A, which has already been adjusted perpendicular to B. The axis of B is maintained in coincidence with the line of reference, and the glass plate is rotated about the axis of C and the images from the two sides adjusted so as to be both bisected by the horizontal spider-line; this is done by using the crystal-adjusting movements



to make one image lie as far above as the other is below, and then adjusting circle C itself until both images come exactly to the spider-line.

The axis of the circle B may be readily brought parallel to the line of reference (the line to which the crystal face is brought perpendicular during crystal measurements), and will coincide with it in two positions when correctly adjusted, the circle B first lying on one and then on the other side of the optical tubes. In either position we may adjust a plane surface, such as one of the surfaces of the parallel-glass plate, perpendicular to the axis of this circle, and if the two images are bisected by the horizontal spider-line the axes of A and B are truly perpendicular.

When the axes of all three circles have been accurately adjusted as regards their direction, they are finally adjusted in absolute position, so that they pass through the same point, the optical centre, which must lie on the line of reference. This is done with the aid of a needle carried on a peg like that of the crystal-holders, in the same manner as has already been described for the adjustment of the ordinary single-circle goniometer in Chapter III. Many useful details as to this process, together with further amplifications of the mode of effecting the directional adjustments already described, will be found in the original memoir (*loc. cit.* pp. 7 to 11).

**Method of using the Three-circle Goniometer.**—The zero readings of the circles A and B require to be determined before commencing measurements with the instrument. The circle A is rotated until the microscope nearest the observer reads exactly  $360^\circ$ . The upper part of the instrument is then rotated until the axis of B coincides with the line of reference and the circle B lies on the other side of the crystal-holder remote from the optical tubes; the parts are then clamped together. Any further necessary correction will only be to the extent of a few seconds. The circle B is then rotated until the axis of the circle C is vertical, and the microscopes for reading circle B are moved until they read as nearly as possible  $360^\circ$  and  $180^\circ$ . A small correction may again be found necessary, but only to the extent of a few seconds.

The mode of using the instrument for the actual measurement of a crystal is similar to that already sketched for the adapted Fuess instrument. The only difference is that the three circles can be utilised to measure greater arcs, owing to the fact that the line of reference is reflected into the central space, the optical tubes themselves being out of the way at the side. A zone of faces exhibiting symmetry, if any be developed on the crystal, is adjusted parallel to the axis of the circle C. To do this the axis of the circle B is brought into coincidence with the line of reference; the axis of C should at the same time be vertical, for then the images obtained by reflection from the faces of the adjusted zone will cross the field horizontally on rotation of this axis, and the adjustment is easier. The zone thus adjusted is termed the "zone of reference." Its angles are measured on the circle C as that circle is rotated (or on A if preferred by reason of its more finely divided scale, C only reading to minutes), the axis of circle B being still coincident with the line of reference. Each reading corresponds to the position in which the particular face is perpendicular to the axis of B, and therefore on rotation of this axis that face remains parallel to its own plane and the image of the signal remains immovable. The faces of this zone may be termed "origins."



The readings of circles A and B respectively for any other face on the crystal give the polar distance  $\rho$  and the azimuth  $\phi$ , measured from the origin and the zone-plane of the zone of reference respectively. The latter would be represented by an actual face if the symmetry were of a tolerably high order, and the measurements would be much facilitated by its development.

From a face of importance with respect to the symmetry as origin, if there be such developed in the zone of reference, the crystal is to be systematically measured, and the positions of the poles of the various faces plotted out on a stereographic projection in the ordinary manner, the zone of reference being the primitive circle.

The stereographic net of Hutchinson (Fig. 52) is very useful for graphically recording the measurements as the work proceeds, the net being placed on the paper on which the drawing is to be made, and the positions of the various poles pricked off on to the paper through the net.

With this three-circle instrument all the various spherical triangles of the stereographic projection may also be experimentally solved, if it be so desired.

**Method and Two-circle Goniometer of V. M. Goldschmidt.**—The unsuitability of the measurements of  $\phi$  and  $\rho$  with the ordinary two-circle goniometer, for the elucidation of the zonal relationships of crystals, are pointed out very clearly by V. M. Goldschmidt<sup>1</sup> of Christiania, in a memoir contributed from the laboratory of Professor von Groth at Munich. He emphasises this unsuitability especially for crystallochemical investigations involving comparisons of the interfacial and interzonal angles of isomorphous series of substances. Yet he considers that if the accurate work possible with the best single-circle goniometers, for complete zones, could be combined with a means of measuring also directly the angles between the zones, instead of having to calculate them from the interfacial angles, and of avoiding several settings of the crystal on the wax of the crystal-holder, an ideal instrument would be obtained. He considers that such a goniometer is afforded by the three-circle goniometer of Herbert Smith, with which one can read off directly not only the angles between all the faces of any zone, but also the mutual angles of inclination between the zones themselves. On account of its complication and costliness, however, he considers it desirable to provide a simpler instrument to carry out essentially the same measurements as those obtainable with the Herbert Smith goniometer. He has caused Fuess, therefore, to construct such an instrument, which is represented in Fig. 372.

It consists of an ordinary Fuess No. 2 goniometer, to which a new attachment is fitted, instead of the ordinary adjusting apparatus. The usual inner vertical axis supports first the centring apparatus of the usual kind, but more rigidly constructed and somewhat larger. On the upper slider is screwed the basal elongated ground-plate of the vertical circle-fitting, the circle  $v$  itself being carried on its bearing at one end of the arm, and a counterpoise  $c$  placed at the other end on the opposite side of the centre. The bearing-fitting of the circle  $v$  is secured to the ground-plate by two screws  $s$ , which permit of the adjustment of the axis of rotation of this circle

<sup>1</sup> *Zeitschr. für Kryst.*, 1912, 51, 28.

truly perpendicular to the axis of the ordinary horizontal circle. The circle  $v$  is divided into half-degrees and with the vernier reads to one minute. The circle may be fixed by the screw  $a$ , and finely adjusted by the screw  $f$ . The axis of this new vertical circle  $v$  carries two mutually perpendicular circular segmental guiding arcs and sliders  $b_1$  and  $b_2$ , divided and reading with verniers to  $5'$ , which replace the ordinary adjusting segments; the crystal is attached by wax in the usual manner to the slider on the outer guiding arc  $b_2$ .

In attaching the crystal, it is arranged so that the normal to the face chosen as pole-face is as nearly as possible parallel to the axis of the vertical circle. One naturally

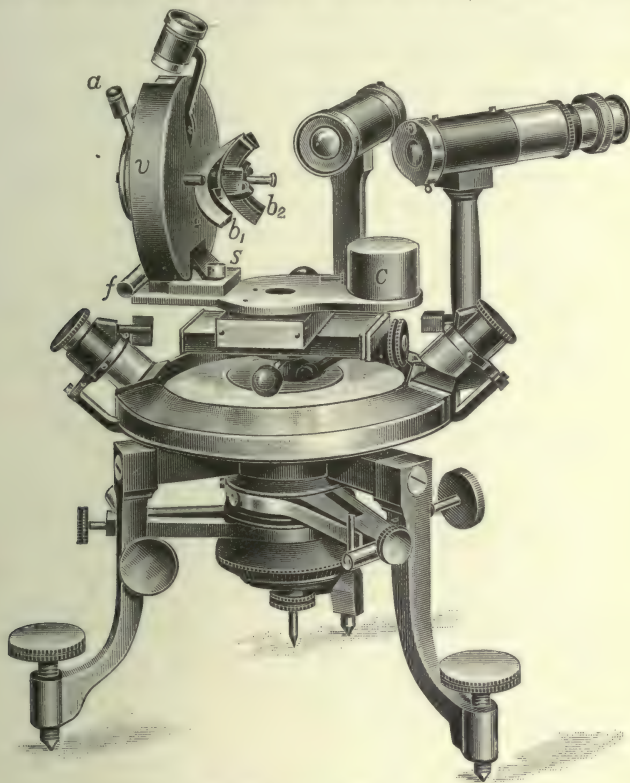


FIG. 372.—V. M. Goldschmidt's Two-circle Goniometer.

chooses as pole-face that face at which the most important zones intersect. During the measurements the telescope and collimator are arranged as close together as possible, so as to command as large a field as possible with the vertical circle. There is then afforded about  $230^\circ$  of play-room.

The polar setting of a face is carried out briefly as follows: One rotates the horizontal circle until the axis of  $v$  is perpendicular to the optic axis of the telescope, and views the crystal through the latter with the aid of the movable lens in front of the objective. The vertical circle is next rotated until one of the adjusting segments (the inner one) becomes vertical, and the other (outer) segment is pushed along the first (inner) one until the desired pole-face appears as a vertical line. The vertical circle is then rotated  $90^\circ$ , until the second (outer) segment stands vertically, and the

crystal-holder is pushed along it until the pole-face again appears as a vertical line. This completes the approximate adjustment.

The fine adjustment is then accomplished as follows: The horizontal circle is rotated until the axis of the vertical circle is symmetrically arranged midway between the optic axes of the telescope and the collimator. The auxiliary lens in front of the objective is pushed out of action, and the reflection of the signal (using the point-signal) from the pole-face is adjusted. The outer segment being arranged vertically one pushes the crystal-holder over it, if necessary, until the signal-image is exactly adjusted to the horizontal spider-line. The vertical circle is then rotated  $90^\circ$ , so that the inner segment stands vertically, and one pushes the outer segment along it, if necessary, until the signal-image again coincides with the horizontal spider-line. The required face is then perfectly adjusted as pole-face.

The various crystal faces may now be measured from the pole-face as origin, while one zone after another is adjusted parallel to the horizontal circle (by simple rotation of the vertical circle). The mutual angles of inclination of the various zones are read off from the vertical circle, while the angles of the faces from the pole-face are read off on the horizontal circle. These latter interfacial angles correspond to the angles  $\rho$  of Professor V. Goldschmidt, while his angles  $\phi$  correspond to the interzonal angles. The only difference between the two methods is that V. Goldschmidt gives the two angles  $\phi$  (azimuth) and  $\rho$  (polar distance) for every face, whereas V. M. Goldschmidt prefers to give the  $\phi$ -value for the whole zone only, while giving the  $\rho$ -values, like his namesake, for every face.

**The Gnomonic Projection.**—In the case of the stereographic projection, which has been so fully described in Chapters IV. and VI., the crystal is imagined to be surrounded by a sphere, and from the common centre of crystal and sphere perpendicular lines are drawn to the crystal faces. The intersection points of these lines with the surface of the sphere are the "poles" of the faces, defining the position of the latter, and to get their stereographic projection we project them on the equatorial plane, regarding this as the plane of the paper, on the supposition that the eye be placed at the north or south pole of the sphere, projection lines joining the eye and the facial poles on the other hemisphere (southern if the eye be at the north pole) passing through the plane of projection at the projections of the poles.

Now there is another mode of projection known as the **gnomonic**, which has been very largely used by Professor V. Goldschmidt and his school at Heidelberg. Whilst in the stereographic projection the point of sight is situated on the surface of the sphere, the gnomonic is a perspective projection in which the eye is supposed to be placed at the centre of the sphere and the poles are projected (the projection lines being the continued radii themselves) on to a tangent plane. Usually the particular tangent plane used as the plane of projection is that at the north pole of the sphere, so that the gnomonic projection plane lies above the stereographic projection plane, and parallel to it, at the height or distance of the sphere's radius. The relations of the two projections (Gn. gnomonic and St. stereographic) are clearly exhibited in Fig. 373, if we use the south pole S for the eye-point of the stereographic. It will be seen that



$\phi$  relatively to the zero meridian  $\phi=0$  remains unchanged in the stereographic and gnomonic projections. The distance of the facial pole  $P'$  from the centre of projection (gnomonic)  $C$  is  $CP' = r \tan \rho$ .

The gnomonic projection is used almost exclusively in connection with two- (or three-) circle goniometry, and is an essential part of the V. Goldschmidt method, which will be more fully dealt with in the succeeding sections.

The lines  $CP'$  and  $OP''$  in Fig. 373, joining the two centres of projection to the two projections (gnomonic and stereographic) of the facial pole  $P$ , are parallel, being the intersections of the two parallel planes of projection with the plane  $CSP$  containing the pole  $P$  (on the surface of the sphere) of the face represented by the little triangle about  $O$ . The centre of the gnomonic projection  $C$  is the point of contact of the tangent plane with the sphere, that is, the point in which a perpendicular from the centre of the sphere meets the touching plane. Another mode of describing the gnomonic projection is that it is the intersection, with the plane of the paper, of the sheaf of lines drawn from a point perpendicularly to the faces of a crystal. Each face is thus represented on the projection by a point, and each zone by a line joining two such points. The plane of the figure is a plane of symmetry, if the crystal belong to any but the monoclinic and triclinic systems.

As the planes of all great circles pass through the centre of the sphere, such great circles representing the zones of faces of the crystal appear as straight lines when projected on the tangent plane. The pole of a face common to two zones is situated consequently at the intersection of the two straight lines representing the zones. The zonal relationships can, therefore, be examined by means of a linear scale, and the anharmonic ratio of four faces in a zone is afforded by the positions of the points representing them on the zonal straight line, as measured on this scale, a considerable advantage. This advantage is greatly enhanced when it is possible to make the north (or south) pole of the sphere the centre of projection, and the basal plane (001) or (0001) the pole-face acting as origin for the measurement of  $\rho$ , as can readily be done in the case of a crystal other than monoclinic or triclinic. Distances (from the centre) of the poles of faces along the various zones are then proportional to  $\tan \rho$ , and the azimuth angles  $\phi$  are the actual angles between the zones, assuming the

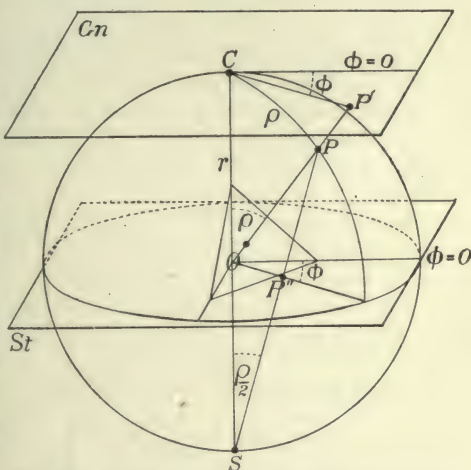


FIG. 373.—Relations of Gnomonic and Stereographic Projections.

face (010) or its equivalent to be the zero (first meridian) for  $\phi$ , as will also usually be possible. But the gnomonic projection has the defect that all facial poles on the great circle parallel to the plane of projection are not projected at all, for their projections would lie at an infinite distance. Indeed  $45^\circ$  of angle on each side is all that can usually be conveniently included in a gnomonic projection, although the extreme limit is generally said to be  $75^\circ$ . Hence, only a portion of the sphere and of the crystal can be represented on the same diagram, and the portion thus represented should be a characteristic one. For this reason the stereographic is a much superior projection for all ordinary purposes. For it gives us a complete plan of the distribution of the faces of a crystal, by solid dots for poles on the upper hemisphere, and by little rings for poles on the lower half, if it be desired to represent the latter distinctively on account of their not all lying on the projection identically with those of the upper hemisphere; and the primitive circle of poles of the zone of faces perpendicular to the plane of projection is obviously the natural boundary of the figure. In the case of the gnomonic projection, however, some arbitrary boundary, such as a square or a circle, has to be given to the figure. Other difficulties are, that the diagram suffers from distortion, owing to linear distances from the centre of projection being tangents of the corresponding angles, and that parallels of latitude on the sphere are projected as conic sections, being only circles when either the north or south pole of the sphere is the centre of projection.

**Relation between the Gnomonic and Orthogonal Projections.**—On the other hand, however, a second advantage, besides suitability for use with a linear scale, is possessed by the gnomonic projection, namely, that a drawing of the crystal in orthogonal projection can readily be constructed from it. For, as the lines in a gnomonic projection are the projections of zone planes, the edges of all faces belonging to any one zone are perpendicular to the line representing it. These perpendiculars

to the gnomonic zone-lines are thus the directions of the orthogonal projections of the edges, the same plane of projection being assumed to be taken for both the gnomonic and the orthogonal projection.

As an illustration of this useful fact, and an example of the gnomonic projection of a typical rhombic crystal (the most general of the rectangular systems), there are given in Figs.

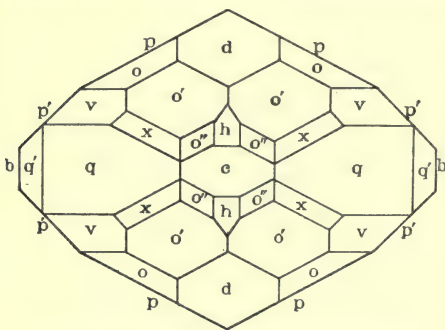


FIG. 374.—Orthogonal Projection of Topaz.

orthogonal projection, the plan regarded from vertically above in the direction of the vertical axis  $c$ , of a topaz crystal investigated by Baumhauer, and the corresponding gnomonic projection of the same crystal. A somewhat similar crystal of topaz has been described and its measurement

detailed in Chapter XV., and its external appearance and stereographic projection are given in Figs. 195 and 196 (pages 231 and 232). The crystal now shown in orthogonal projection in Fig. 374 exhibits all the forms developed on the crystal portrayed in Fig. 195, and the author's lettering

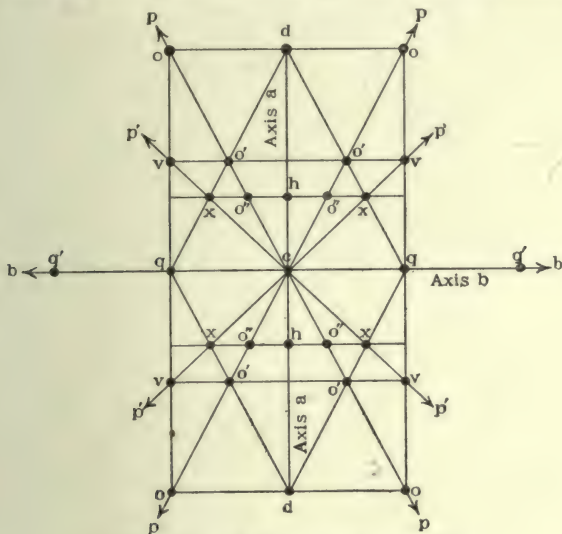


FIG. 375.—Gnomonic Projection of Topaz.

of the faces and forms is preserved, as given in Fig. 195; in addition, however, the crystal orthogonally represented in Fig. 374 is richer in faces by four forms,  $b = \{010\}$ ,  $d = \{101\}$ ,  $h = \{103\}$ , and  $v = \{122\}$ . All but the last mentioned,  $v$ , are shown in the stereographic projection, Fig. 196.

The gnomonic projection, Fig. 375, shows the poles of all the forms except those of the prismatic zone,  $b = \{010\}$ ,  $p = \{110\}$ , and  $p' = \{120\}$ , which can only be indicated by direction arrows, terminating the cross-zones containing these poles and the centre of projection, the pole of  $c = (001)$ , owing to the characteristic inability of this projection to represent poles of faces inclined at more than  $75^\circ$  (at most) from the basal plane. It will be clearly apparent that each straight line representing

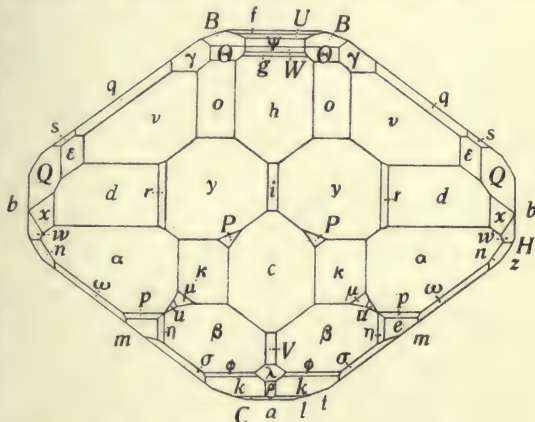


FIG. 376.—Orthogonal Projection of Colemanite.



a zone on the gnomonic projection is perpendicular to the directions in the orthogonal projection of all the parallel edges between the various faces of the zone in question.

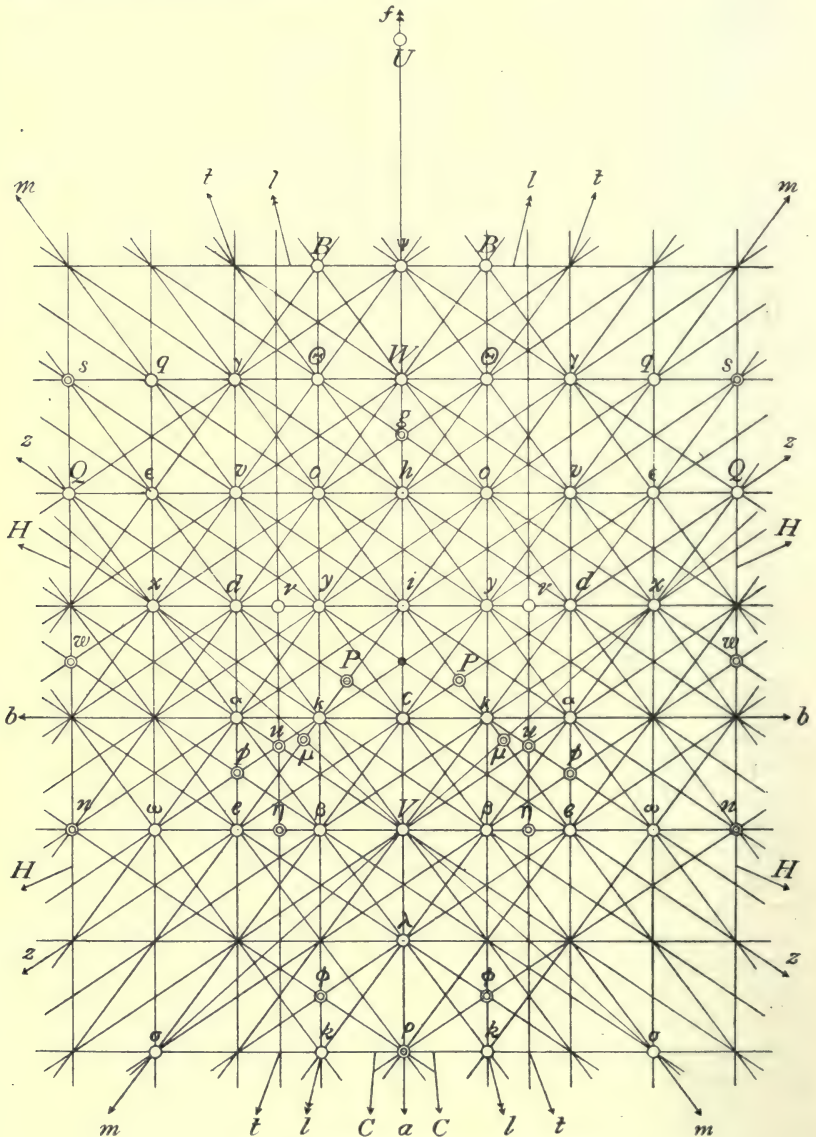


FIG. 377.—Gnomonic Projection of Colemanite.

A second example may be given, taken from the monoclinic system. The crystal selected is one of colemanite, the most beautiful of the mineral

borates,  $\text{HCa}(\text{BO}_2)_3 \cdot 2\text{H}_2\text{O}$ ; the crystals of this mineral much resemble those of calcite in appearance, often exceeding two or three inches in size, but exhibiting a more adamantine lustre. The mineral was first discovered in California in the year 1882, and was measured by A. W. Jackson in 1885. It was more fully investigated by A. S. Eakle<sup>1</sup> in 1902, and the three figures 376, 377, and 378 are reproduced from his memoir. Fig. 376 is an orthogonal projection of a typical crystal of colemanite, Fig. 377 is the corresponding gnomonic projection, and Fig. 378 represents one of the actual crystals measured by Eakle. The orthogonal projection is an idealised one, combining all the forms observed by Eakle after measuring a large number of crystals, so that the corresponding gnomonic projection also exhibits the poles of all the forms observed. The perpendicular relationship between the interfacial edges of the orthogonal projection in Fig. 376 and the corresponding zone-lines of the gnomonic projection in Fig. 377 will be obvious on looking through the page against a bright light, the two figures being printed back to back. In the case of colemanite the basal plane  $c=(001)$  is actually developed, but as the system of symmetry is monoclinic the pole of the face  $c=(001)$  does not occupy the centre of the projection, which is marked by the black central dot in Fig. 377, as it does in that of the orthorhombic topaz projected gnomonically in Fig. 375.

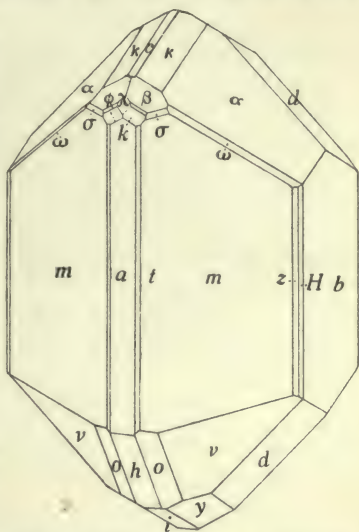


FIG. 378.—Measured Crystal of Colemanite.

**V. Goldschmidt's Notation and Formulæ and their Use.**—In his combination of two-circle goniometry with the use of the gnomonic projection Professor V. Goldschmidt employs an abbreviation of the Millerian indices, in which two of the three indices  $hkl$  only are used and are termed  $p$  and  $q$ . He makes the last Millerian index  $l$  equal to unity, and then eliminates it altogether. Thus the Millerian (522) would become  $\frac{5}{2}1$ . He considers

that the zonal relationships are better thus expressed by two symbols, because all forms having the same  $p$  or  $q$  lie in the same zone. Thus the forms  $\frac{5}{4}\frac{3}{2}$ ,  $\frac{1}{3}\frac{3}{2}$ ,  $\frac{4}{5}\frac{3}{2}$  are tautozonal, yet the corresponding Millerian indices (564), (296), and (8.15.10) would not suggest this.

Now the plane of gnomonic projection, the tangent plane to the sphere at the north (or south) pole is usually and preferably taken as perpendicular to the prismatic zone, so that the centre of projection is, as already mentioned, identical with the pole of the basal plane if the crystal belong to one of the rectangular systems, the rhombic for

<sup>1</sup> Univ. of Calif. Bull. Geol., 1902, 3, 40.





the gnomonic projection, as further indicated in Fig. 379. The values of these rectangular co-ordinates in terms of the angular co-ordinates are readily obtained from the right-angled triangle itself, of which  $x'$ ,  $y'$ , are the two sides and  $d'$  ( $=\tan \rho$ ) is the hypotenuse; for  $\frac{x'}{d'} = \sin \phi$ , and  $\frac{y'}{d'} = \cos \phi$ ; so that

$$x' = \sin \phi \tan \rho, \text{ and } y' = \cos \phi \tan \rho.$$

Hence, from the measurements of  $\phi$  and  $\rho$  for all the faces of the crystal, the rectangular co-ordinates of these faces can be obtained and their poles directly plotted on squared paper, as a preliminary to the construction of the proper gnomonic projection. Also the measured (on the graph) co-ordinates  $x'$  and  $y'$  of any other face which is located graphically, say by its presence at the intersection of two zones, afford the true position of that face in terms of the  $x'$  and  $y'$  of the parametral form  $pq$ .

For monoclinic crystals, when the pole of  $c=(001)$  lies at a distance  $e'=\tan \rho$  in front of the centre of projection S, the distances  $p_0'$  and  $q_0'$  are the co-ordinates for the parametral pyramid  $pq$ ; and for any value of  $pq$  we have the rectangular co-ordinates  $x'=pp_0'+e'$  and  $y'=qq_0'$ .

**Example of Investigation of a Monoclinic Crystal by the Two-circle Method.**—In order to render these facts and the procedure clear for the more difficult case of oblique crystals, the monoclinic crystals of colemanite (Figs. 376, 377, and 378) measured by Eakle (*loc. cit.*) may be taken as a typical example. An average of twenty measurements of the polar distance  $\rho$  for the basal pinakoid  $c=(001)$  gave  $20^\circ 7'$ , the azimuth  $\phi$  being  $90^\circ 0'$ . Therefore, its distance on the gnomonic diagram (Fig. 377) in front of the centre of projection S was  $e'=\tan 20^\circ 7'=0.3663$ . The same value was given by the co-ordinate  $x'$  for the clinodomes  $\kappa=(011)$  and  $\alpha=(021)$ , for  $x'=e'$  for these forms, as will be clear from the gnomonic diagram 377, in which  $c$ ,  $\kappa$ , and  $\alpha$  are all on the same horizontal line representing the zone  $[(001) \cdot (010)]$ . The mean of 44 values of  $x'$  for these domes 01 and 02 (using Goldschmidt's  $pq$  symbols) gave  $x'=0.3663$ .

The axial angle  $\beta$  is also directly given, as will be clear from the little secondary diagram in Fig. 379; for  $e'=\cot \mu$ , from which  $\mu=69^\circ 53'$  and  $\beta=180^\circ-\mu=110^\circ 7'$ .

The next step was to calculate the rectangular (gnomonic) co-ordinates  $x'$  and  $y'$  for all the various faces developed on the crystals, from the measured angular co-ordinates  $\phi$  and  $\rho$  and the formulæ  $x'=\sin \phi \tan \rho$ ,  $y'=\cos \phi \tan \rho$ . For the positive forms  $pp_0'=x'-e'$ , and for the negative forms  $pp_0'=x'+e'$ . As the symbols  $pq$  are simple multiples of the co-ordinates  $p_0' q_0'$  of the unit parametral form, the values  $p_0' q_0'$  for each form were readily deduced. The mean values of  $p_0'$  and  $q_0'$  for 15 crystals were 0.7443 and 0.5430. Even for a monoclinic crystal the latter value is actually the axial ratio  $c:b$ ; but the axial ratio  $a:b$  is not the former value, as the axis  $a$  is inclined and may be written  $\hat{a}$ . Its true value  $\frac{\hat{a}}{b} = \frac{\hat{a}}{\sin \mu}$ , in which  $\hat{a}$  is the value for a rectangular  $a$ -axis.

Hence, the desired true  $\hat{a}$ -axial value is  $\hat{a} = \frac{q_0'}{p_0' \sin \mu}$ , from which the value 0.7768 for  $\hat{a}$  was obtained.

Thus the elements of colemanite were found to be  $a:b:c=0.7768:1:0.5430$ , and  $\beta=110^\circ 7'$ .

That the value last given for  $\hat{a}$  is correct, will be seen from the following considerations. To determine the polar elements  $p_0, q_0$ , and  $e$ , it has to be remembered that the values  $p'_0, q'_0$ , and  $e'_0$  are the elements when  $h=1$  and  $r_0=\frac{1}{\sin \mu}$ . Hence, when  $r_0=1$  these values have to be multiplied by  $\sin \mu$  in order to obtain the polar elements. Thus  $p_0=p'_0 \sin \mu$ ,  $q_0=q'_0 \sin \mu$ , and  $e=e'_0 \sin \mu=\cos \mu$ . For colemanite the elements become  $p_0=0.6989$ ,  $q_0=0.5098$ ,  $e=0.3439$ . To get the true axial ratio  $a:b:c$ , in the rectangular axial systems,  $q'_0=\tan(001:011)$  and  $p'_0=\tan(001:101)$ ; and, as  $b=1$ , for such systems  $c=q'_0$  and  $\hat{a}=\frac{c}{p'_0}=\frac{q'_0}{p'_0}$ . For monoclinic crystals  $c$  remains  $=q'_0$ , but the clino-axis  $\hat{a}$  is equal to  $\frac{\hat{a}}{\sin \mu}$ , so that  $c=q'_0=\frac{q_0}{\sin \mu}$  and  $\hat{a}=\frac{q'_0}{p'_0 \sin \mu}=\frac{q'_0}{p_0}=\frac{q_0}{p_0 \sin \mu}$ . The values of  $c$  and  $\hat{a}$  for colemanite were thus found, as above stated, to be  $\hat{a}=0.7768$  and  $c=0.5430$ .

In the following table are given the results of Eakle for the positions of 21 of the principal faces of the crystals of colemanite, as shown in Figs. 376 and 378. It will afford some indication of the usual mode of recording (1) the results of the measurements of azimuth  $\phi$  and polar distance  $\rho$ , and (2) the calculations of the rectangular co-ordinates  $x'$  and  $y'$ .

Face.	Symbol.		$\phi$ .	$\rho$ .	$x'$ .	$y'$ .
	Goldschmidt.	Miller.				
$c$	0	(001)	$90^\circ 0'$	$20^\circ 7'$	0.3663	0
$b$	$0\infty$	(010)	0 0	90 0	0	$\infty$
$a$	$\infty 0$	(100)	90 0	90 0	$\infty$	0
$m$	$\infty$	(110)	53 53	90 0	1.3709	$\infty$
$t$	$2\infty$	(210)	69 58	90 0	2.7419	$\infty$
$z$	$\infty 2$	(120)	34 26	90 0	0.6854	$\infty$
H	$\infty 3$	(130)	24 33	90 0	0.4570	$\infty$
$\kappa$	01	(011)	34 0	33 13	0.3663	0.5430
$\alpha$	02	(021)	18 18	48 54	0.3663	1.0860
$\lambda$	+20	(201)	90 0	61 40	1.8549	0
$i$	-10	( $\bar{1}$ 01)	90 0	20 42	0.3781	0
$h$	-20	(201)	90 0	48 18	1.1223	0
$\beta$	+1	(111)	63 56	51 2	1.1106	0.5430
$y$	-1	( $\bar{1}$ 11)	34 51	33 29	0.3781	0.5430
$d$	-12	( $\bar{1}$ 21)	19 11	48 59	0.3781	1.0860
$x$	-13	( $\bar{1}$ 31)	13 4	59 7	0.3781	1.6290
$v$	-2	(221)	45 56	57 22	1.1223	1.0860
$\omega$	+13	(131)	34 17	63 6	1.1106	1.6290
$o$	-21	(211)	64 11	51 16	1.1223	0.5430
$k$	+31	(311)	78 12	69 22	2.5992	0.5430
Q	-24	( $\bar{2}$ 41)	27 19	67 45	1.1223	2.1720

**Example of Gnomonic Projection of a Trigonal Crystal very rich in Faces.**—Perhaps the best example that could be given, of the gnomonic

projection of a crystal very rich in faces, is that of the two isomorphous red silver minerals proustite,  $\text{Ag}_3\text{AsS}_3$ , and pyrargyrite,  $\text{Ag}_3\text{SbS}_3$ , drawn by Sir Henry Miers, who in the years 1886 and 1887 made a detailed investigation<sup>1</sup> of these remarkable minerals. They crystallise in the ditrigonal polar class 20 (hemimorphic hemihedral) of the trigonal system, the same class as tourmaline. The minerals form exceptionally beautiful crystals, the hexagonal prism of the second order  $\{10\bar{1}\}$  being always a prominent form, terminated by the semi-forms of the primary and other rhombohedra, scalenohedra, and various pyramids; the two ends of the crystals are quite different in accordance with the polar hemimorphic symmetry, both semi-forms of any holohedral form being rarely developed to the same extent, if both be present at all, at the two ends of the vertical axis. Fig. 380, which may represent either mineral, is reproduced from the memoir of Miers, and gives a general idea of the main forms developed, some of which are more particularly characteristic of proustite, and others of pyrargyrite. Many of the crystals are exceedingly rich in faces, as will be best appreciated from the reproduction of Miers' gnomonic projection given in Fig. 381, which shows all that it is possible to record on such a projection of the 145 forms discovered after an investigation of numerous crystals by Miers and many previous observers.

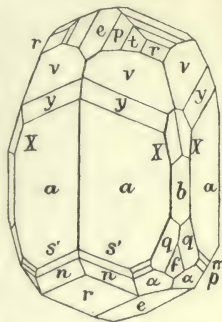


FIG. 380.—Crystal of Red Silver Ore.

The following are the indices of the forms actually shown on the crystal represented in Fig. 380, the first nine being arranged in order of frequency of development :

$a = \{10\bar{1}\}$	$y = \{30\bar{2}\}$
$e = \{110\}$	$f = \{223\}$
$q = \{324\}$	$n = \{40\bar{1}\}$
$b = \{2\bar{1}\bar{1}\}$	$X = \{834\}$
$v = \{20\bar{1}\}$	$\alpha = \{423\}$
$t = \{310\}$	$\rho = \{643\}$
$r = \{100\}$	$\pi = \{19.11.1\bar{2}\}$
$p = \{210\}$	

The gnomonic projection, Fig. 381, also represents both minerals, and is drawn so that the figure is the intersection of the face-normals by a plane inclined at  $54^\circ 44\frac{1}{2}'$  to the vertical axis, at  $45^\circ$  to two adjacent lateral axes, and at a distance of  $b^* = 84.85$  mm. from the origin, where \* is the projection of its own normal (passing through the centre of the imaginary sphere) on the plane of the figure. It includes one  $60^\circ$ -sector of the stereographic projection, formed by the three faces  $o = (111)$ ,  $b = (2\bar{1}\bar{1})$ , and  $b = (11\bar{2})$ .

When the crystals are freshly obtained from the dark recesses of the silver mine they are very lustrous and transparent, but they are rapidly affected by the actinic rays of light, like so many other of the compounds of silver, and require to be stored in the dark. One of the

<sup>1</sup> *Min. Mag.*, 1887, 7, 145; 1888, 8, 37.





dark case. It possesses a beautiful scarlet-vermilion colour, and affords a bright red "streak" (colour of the powder on scratching or pulverising). (Pyrargyrite is generally dark grey in appearance, and yields a reddish-purple streak.) The two terminations are different, clearly exhibiting the hemimorphism.

The angles are so similar that the gnomonic projection in Fig. 381 represents both minerals practically accurately, on the scale of the drawing, but they are not identical. The rhombohedral angle of proustite is  $72^{\circ} 12'$ , and that of pyrargyrite  $71^{\circ} 22'$ . Further reference to this slight but real difference in such angles as are not fixed by the symmetry will be found in Chapter LIV., in considering the nature of isomorphism.

**Fundamental Propositions concerning the Gnomonic Projection.**—The following four propositions are given and proved by Miers in the 1887 memoir just quoted. It should be understood that the plane of projection must cut the whole group of normals enclosed within three of the principal planes of symmetry, in the cases of all crystals belonging to the five higher systems of symmetry (that is, not monoclinic or triclinic).

1. If OX, OY, OZ in Fig. 382 be any three normals, the angles between which are  $YOZ = \xi$ ,  $ZOX = \eta$ ,  $XOY = \zeta$ ; and if OP be drawn normal to the plane of the figure XYZ, and the angle  $POX = \alpha$ ,  $POY = \beta$ , and  $POZ = \gamma$ ; then, if  $OP = p$ ,

$$PX = p \tan \alpha, \quad PY = p \tan \beta, \quad PZ = p \tan \gamma.$$

The triangle XYZ can thus be drawn, and the position of P be laid down for any position of the plane of the figure, at any required distance

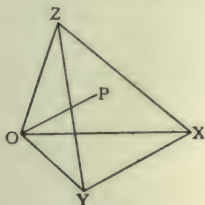


FIG. 382.

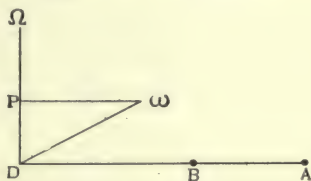


FIG. 383.

$p$  from the origin. Any other point of the system being then laid down from its known angles, the whole system of points corresponding to possible crystal faces may be mapped out by the intersections of lines joining the points.

The dihedral angles are measured on the projection by means of the "Circle of Projection" described from centre P with radius equal to  $p$ .

2. To find the angle between two normals the projections of which are AB, Fig. 383. Through P draw PD perpendicular to AB, meeting AB produced in D. Draw Pω parallel to AB, meeting the circle of projection in ω. Along PD (produced if necessary) take  $P\Omega = D\omega$ . Then the angle between any pair of normals the projections of which AB lie in the zone line ABD is the angle subtended by AB at Ω.

3. To find the angle between two zones the projections of which are CA, CB, Fig. 384.

Join CP; draw  $P\omega$  perpendicular to CP, meeting the circle of projection in  $\omega$ . Join  $C\omega$ ; draw PD perpendicular to  $C\omega$ , and in PC take

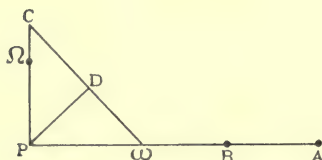


FIG. 384.

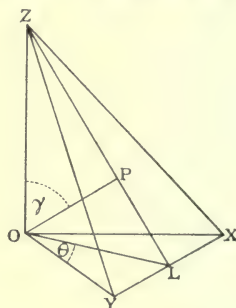


FIG. 385.

$P\Omega = PD$ . Then the angle between any pair of zones the projections of which CA, CB, intersect in the point C is the angle subtended at  $\Omega$  by their intersections with  $P\omega$  produced.

The preceding three rules enable any crystal to be readily projected. The following fourth proposition enables considerable simplification to be effected in the cases of crystals with rectangular, hexagonal, or trigonal axes, a convenient choice of plane of projection being of course assumed.

4. If OX, OY, OZ, Fig. 385 be the rectangular axes of the  $90^\circ$ -systems, or two of the lateral axes and the vertical axis of the two  $60^\circ$ -systems; and if ZP meet XY in L; then  $ZLX = 90^\circ$ .

It may then be proved that :

$$(a) \quad \frac{LX}{LZ} = \tan \theta \cdot \cos \gamma, \text{ where } \theta = \frac{\zeta}{2};$$

$$(b) \quad PL = ZL \cos^2 \gamma;$$

$$(c) \quad p = \frac{PZ}{\tan \gamma} = \frac{PX}{\tan \alpha}.$$

The triangle XYZ may be drawn from (a), the point P may be projected from (b), and the circle of projection may be described from (c). Now in the cubic, tetragonal, and rhombic systems  $\theta = 45^\circ$ . Hence, if also  $\gamma = 45^\circ$ ,  $\cos \alpha = \frac{1}{2}$ , then

$$\frac{LX}{LZ} = \frac{1}{\sqrt{2}}, \quad PL = \frac{ZL}{2}, \quad p = PZ.$$

In the hexagonal and trigonal systems  $\theta = 30^\circ$ , and if  $\cos \gamma = \frac{1}{\sqrt{3}}$ ,  $\cos \alpha = \frac{1}{\sqrt{2}}$ , and  $\alpha = 45^\circ$ , then

$$\frac{LX}{LZ} = \frac{1}{3}, \quad PL = \frac{ZL}{3}, \quad p = PX.$$

**Special Use of the Gnomonic Projection in Three-circle Goniometry.**—The gnomonic projection is particularly useful in connection with the



employment of a Herbert Smith three-circle goniometer. For such a projection can well be made to represent most of the poles, if not all, investigated for one setting of the crystal on the wax of the crystal-holder. The measurements are made from poles in a certain zone, the zone of reference, as origins, and from the readings of the circle from these poles we obtain for any other pole its distance from the origin and its azimuth from the zone of reference. These co-ordinates are then used, as in two-circle goniometry, to locate the poles of the faces on the gnomonic diagram, the plane of which is taken at right angles to the edge (axis) of the zone of reference. As poles in this zone are projected to infinity, all zones passing through the same origin (a pole on the zone of reference) appear as parallel lines on the projection.

This will be rendered clearer by reference to Fig. 386, in which P is the pole of the zone of reference, and Z the direction of the origin-pole on this zone of reference. If we draw PX at right angles to PZ, and then if Q be any point (a facial pole for instance) and we draw Qk parallel to PZ, Qk will be the projection of the zone passing through Q and the origin Z. Herbert Smith,<sup>1</sup> to whom this and the next three figures are due, in applying the projection to work with his three-circle goniometer described earlier in this chapter, has shown that the linear co-ordinates of the gnomonic projection are related to the spherical co-ordinates of the stereographic projection by two simple equations. If Qk in Fig. 386 be the linear distance of the point Q, which may be assumed to be a facial pole, and  $\rho$  and  $\phi$  the spherical co-ordinates of the pole Q with respect to the origin Z,  $\rho$  being the distance from Z and  $\phi$  the azimuth from the zone of reference, then :

$$Qk = r \cot \rho \operatorname{cosec} \phi, \text{ and } Pk = r \cot \phi.$$

In order to facilitate the plotting of linear distances on the gnomonic projection and the graphical solution of angles therewith, Herbert Smith gives in the same memoir the design of a protractor, shown in Fig. 387, and also a table of values of  $\cot \rho \operatorname{cosec} \phi$  for angles from  $25^\circ$  to  $90^\circ$ . The angles between poles or zones may thus be rapidly graphically determined from the projection with the aid of the protractor and table.

The protractor is a strip of celluloid on which is engraved a semi-circle, the diameter of which is on the edge of the strip; both the diameter and the radius at right angles to it are divided into millimetres, while the semicircle is divided into half-degrees. By means of the two rectangular scales the poles can easily be plotted from their plane

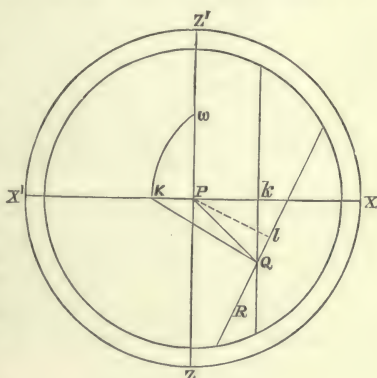


FIG. 386.

<sup>1</sup> *Mineralogical Magazine*, 1903, 13, 309.

co-ordinates. It is most convenient in work with two- or three-circle goniometers to take the centre of projection itself as origin, the azimuths being then the same as the plane angles, and the linear distances proportional to the tangents of the corresponding angles.

In Fig. 388 are represented a series of poles lying in four zones passing through the same origin in the zone of reference, and therefore represented

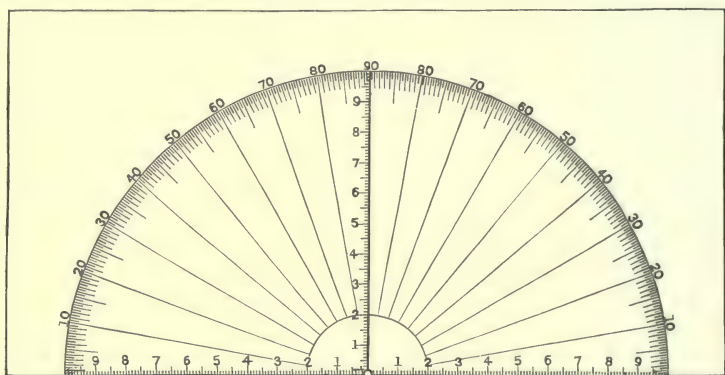


FIG. 387.—Herbert Smith's Gnomonic Protractor.

by straight lines parallel to each other in the gnomonic projection; their azimuths may be indicated by  $\phi$ ,  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$ . It will then be an important fact that the following relationship holds, namely:

$$\frac{km \cdot \ln}{kl \cdot mn} = \frac{(\cot \phi_2 - \cot \phi)(\cot \phi_3 - \cot \phi_1)}{(\cot \phi_1 - \cot \phi)(\cot \phi_3 - \cot \phi_2)} = \frac{\sin(\phi - \phi_2) \sin(\phi_3 - \phi_1)}{\sin(\phi - \phi_1) \sin(\phi_3 - \phi_2)} = \text{a rational quantity.}$$

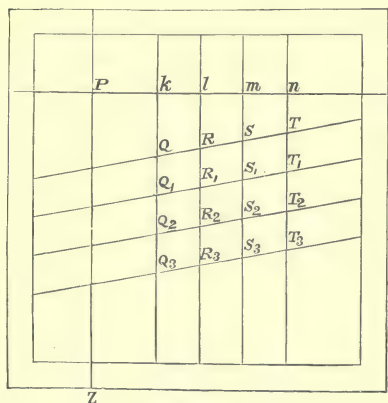


FIG. 388.

This rational quantity is the anharmonic ratio of four crystallographically possible zones, intersecting in the same pole.

If we suppose  $[TT_1T_2T_3]$  to be the zone of reference  $n$  lies at infinity, and we have the simple relation left that

$$\frac{km}{kl} = \text{a rational quantity.}$$

A quite similar relation holds with respect to the poles themselves in the various zones, so that, for instance, we have:

$$\frac{QQ_2}{QQ_1} = \text{a rational quantity.}$$

Under these conditions the principal zones in the diagram are equally spaced apart, and a network of parallelograms is produced as in Fig. 388.

In special cases rectangles and squares are afforded. Hence also unit linear distances on parallel lines must be the same, so that we have only to take measurements on the diagram in order to determine the simple indices corresponding to any particular face.

Two simple problems are of constant recurrence, namely, those already stated on page 479 (Propositions 2 and 3), and it may be of use to indicate how they may be solved graphically with the aid of the protractor and table.

(1) **To find the Angle between Two Poles represented by Points on the Gnomonic Projection.**—Suppose Q and R in Fig. 386 to be the poles. The protractor is placed so that the diametral scale lies along QR while the radial scale at right angles to the diameter passes through the centre of projection P. The zero of both scales will lie on  $l$ . Readings of the scales are then taken for the points P, Q, and R. The reading for P obviously gives the length  $Pl$ , and from the table the azimuth of the zone QR can be found. We can then further find from the table, with the aid of this information, the angular distances corresponding to the observed lengths  $Ql$  and  $Rl$ . The required angle or its supplement is then either the sum or the difference of these two angles  $Ql$  and  $Rl$ , according as Q and R lie on opposite sides or the same side of  $l$ . In the case shown in Fig. 386 the difference is taken, as both Q and R lie on the same side of  $l$ , and the angle obtained is the actual angle required. When Q and R lie on opposite sides of  $l$  the sum gives the supplement of the angle required, because the table gives the distance measured from the origin in the zone of reference.

(2) **To find the Angle between any Two Zones, represented by Straight Lines on the Gnomonic Projection.**—In order that this problem may be

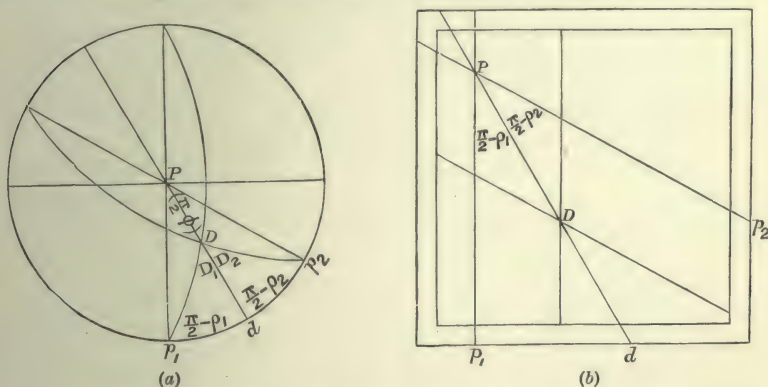


FIG. 389.—(a) Stereographic Projection ; (b) Gnomonic Projection.

better understood, both the stereographic and gnomonic projections are given side by side at a and b in Fig. 389. The two zones intersect in D and meet the zone of reference in  $p_1$  and  $p_2$ ; the zone PD is also drawn, meeting the zone of reference in  $d$ .

Assuming the angle  $Dd$  to be  $\phi$ , the angles  $p_1d$  and  $p_2d$  to be the



complements of  $\rho_1$  and  $\rho_2$ , and the angles  $p_1Dd$  and  $p_2Dd$  to be  $D_1$  and  $D_2$  respectively, we then have in the triangles  $p_1Dd$  and  $p_2Dd$ :

$$\tan D_1 = \cot \rho_1 \operatorname{cosec} \phi, \text{ and } \tan D_2 = \cot \rho_2 \operatorname{cosec} \phi.$$

The protractor is now placed on the gnomonic diagram so that the zero of the linear scales is on D while the radial scale passes over P the centre of projection. The reading for P on this  $90^\circ$ -radius scale is taken, and also the readings of the two zone-lines on the circular scale; from the first we obtain the length PD, and therefore as before in case (1) from the table we find the angle  $\phi$ , while from the other two we obtain the angles  $\rho_1$  and  $\rho_2$ . Treating  $\phi$  as an azimuth and  $\rho$  as a distance we get from the table a corresponding quantity, which from the first column of the table we convert into the complement of  $D_1$  or  $D_2$ , as this column gives the cotangents. The sum or difference must be again taken as in problem (1), according as the angles have been measured on opposite sides or the same side of PD. The latter case affords the required angle itself, while the former gives the supplement, as in the case of problem (1).

These aids to the use of the gnomonic projection introduced by Herbert Smith, from whose memoir most of the foregoing rules for their application are taken, have greatly simplified the use of the projection, and thus indirectly rendered a still further service to three-circle goniometry. The protractor is made by Mr. Steward of the Strand, and is a very convenient accessory to possess in any case. The table of cosecant azimuths and cotangent distances is too long for reproduction here, and reference should be made to the original memoir in the *Mineralogical Magazine* (*loc. cit.*). An ordinary table of tangents and cosecants enables the protractor to be also applied to any stereographic projection.

**Construction of Clinometric Projection from the Gnomonic.**—A simple method of constructing the ordinary clinometric (parallel perspective) drawing of a crystal from the gnomonic projection, with the aid of an orthogonal projection (plan) first drawn from the latter, has been developed by V. Goldschmidt,<sup>1</sup> and some examples of its use have more recently been given by Miss Mary Porter,<sup>2</sup> Lady Carlisle Research Fellow of Somerville College, Oxford. One of these, a tetragonal (holohedral, class 15) crystal of idocrase (vesuvianite), is illustrated in Fig. 389*a*, the gnomonic projection being on the left and the orthogonal plan and parallel perspective drawing on the upper and lower right respectively.

Idocrase is essentially a silicate of aluminium and calcium, but with many vicarious isomorphous replacements, especially by iron and magnesium. The simplest possible formula is given by von Groth<sup>3</sup> as  $\text{AlCa}_2(\text{OH})\text{Si}_2\text{O}_7$ , the water present being combined and not water of hydration. The crystals from Monte Somma, Vesuvius, are usually brown, but better formed crystals from Ala in Piedmont are green. The idocrase crystal shown in Fig. 389*a* is similar to a beautiful brownish-green one measured by the author, the forms present being the second order tetragonal prism  $a$  {100}, the first order prism  $m$  {110}, and primary pyramid

<sup>1</sup> *Zeitschr. für Kryst.*, 1891, 19, 352.

<sup>2</sup> *The American Mineralogist*, 1920, 5, 89.

<sup>3</sup> *Chemische Kristallographie*, vol. ii. p. 277.

$p\{111\}$ , and the basal pinakoid  $c\{001\}$ . According to Miers<sup>1</sup> the axial ratio is  $a : c = 1 : 0.5373$ , and the two principal angles  $pp = (111) : (\bar{1}\bar{1}\bar{1}) = 50^\circ 40'$  and  $cp = (001) : (111) = 37^\circ 14'$ . These angles on the author's crystal measured  $50^\circ 39'$  and  $37^\circ 16'$  respectively. The more largely developed first order prism  $m$  is nearly a centimetre square; all the prism faces are striated, as usual on idocrase, parallel to the vertical axis  $c$ , but the terminal faces are beautifully plane polished and transparent.

Besides the gnomonic and orthogonal projections only two further accessories are required, the Guide Line (Leitlinie) and Angle Point (Winkelpunkt), and Goldschmidt gives the following instructions for their derivation, which the author has illustrated in Fig. 389a, by adding the

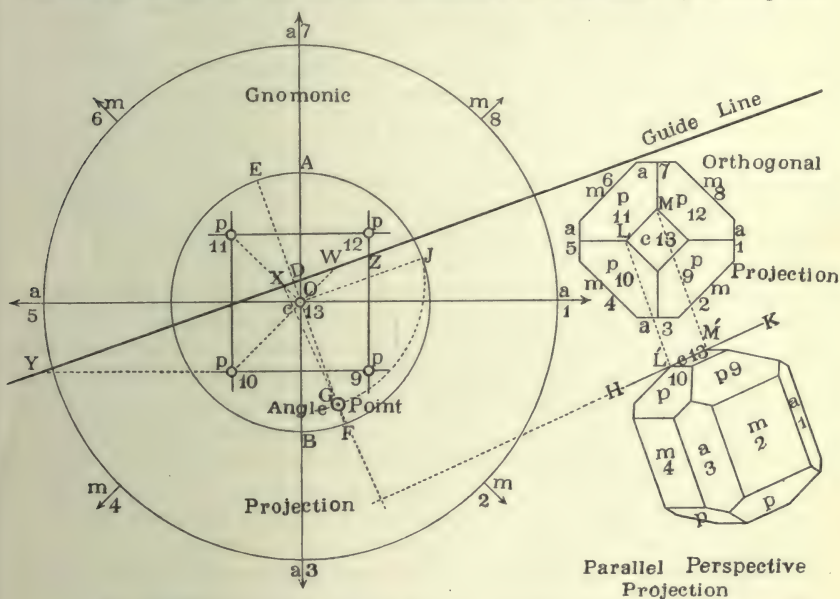


FIG. 389a.—Derivation of a Parallel Perspective Drawing of Idocrase from its Gnomonic Projection.

necessary lines to Miss Porter's figure, and redrawing and relettering the whole. The drawing has been slightly reduced in the reproduction, Fig. 389a.

A vertical diameter AB is drawn to the inner (5 cm. unit) circle, and from B a chord BF is laid off to the right, equal to  $\frac{1}{3}$ rd the radius OB. Next, the further diameter FOE is drawn, and OD taken along OE equal to  $\frac{1}{6}$ th of OB. A line drawn through D perpendicular to FOE, and produced across the whole width of the figure, is then the required guide line.

A radius OJ is then drawn parallel to the guide line, and a circular arc is drawn with D as centre and DJ as radius, to cut the radius OF; the point G where this intersection occurs is the angle point required.

Proceeding now to use the gnomonic projection, with the guide line

<sup>1</sup> *Mineralogy*, p. 494.

and angle point thus obtained, for the drawing of the idocrase crystal, the orthogonal plan is first drawn closely beneath the guide line as produced on the right. An arbitrary selection is then made of a crystal edge with which to commence the parallel perspective drawing, say the edge between the first order pyramid *p*-face 11 and the basal *c*-plane 13. To find its direction we note where the zone [11 : 13], dotted in the gnomonic projection, cuts the guide line, namely at X, and then join X to the angle point; the perpendicular to the line so obtained and produced is the direction HK of the edge 11-13 in question. Its length,  $L'M'$ , is determined by dropping projectors perpendicular to the guide line from its ends L, M, in the orthogonal plan, on to the line HK. A similar procedure is then adopted for the *pc* edge 10-13, the dotted zone containing these faces cutting the guide line at W, and the required edge direction being perpendicular to the line WG joining W and the angle point. Similar constructions for the other two *cp* edges 9-13 and 12-13 complete the basal plane *c*-face 13. We may then pass to the pyramid edge between the *p*-faces 9 and 10, the zone in this case intersecting the guide line at Y, and the edge direction being perpendicular to YG; then similarly for the edge between *p*-faces 9 and 12.

To find the edge between a pyramid end-face and a prism face, say *ap*, 9-3, we lay one side of a set square along the direction line (in the gnomonic projection) of the second order prism *a*-face 3, indicated by the arrow, move it parallel to itself (by sliding against the second set square) until it passes through the pole of the *p*-face 9, and note the point Z where this line cuts the guide line; the perpendicular to the line joining Z and the angle point G is then the required direction of the edge 9-3. We may then similarly find the edge between the pyramid *p*-face 9 and the first order prism *m*-face 2, when X will again be the point on the guide line. Likewise for the edge *ap* between the second order prism *a*-face 1 and the first order pyramid *p*-face 9, thus completing face 9. In like manner all the rest of the faces can be drawn, in order to complete the whole parallel perspective drawing of the crystal.

It will be observed that the relative development of the faces of the crystal in this clinometric drawing will depend on the relative dimensions given to them in the orthogonal plan, except as regards the length of the prism faces, which is obviously not indicated in a plan. The orthogonal projection, therefore, should be drawn so as faithfully to reproduce the relative development of the various faces as far as is possible in a plan.

#### **Concluding Remarks concerning Two- (or Three-) circle Goniometry.—**

The measurement of crystals by the theodolitic two-circle method, that of determining two angular co-ordinates, the azimuth  $\phi$  and polar distance  $\rho$ , has lately become very widely adopted, largely due to the teaching of Professor V. Goldschmidt and to the researches of Fedorov, and is doubtless of great value for rapid work. In particular is this so in connection with the practical operations necessary for the crystallo-chemical analysis of Fedorov which will be found referred to in Chapter XXXIV. That very rapid work, which alone is necessary for the purpose of identifying a crystal as being that of a particular substance, is more readily possible by the theodolite method than with the single-circle goniometer is fully



recognised, and for that reason so much space has been accorded to the description of the method in this chapter. But an emphatic warning is necessary as to its over-use and misuse, the pitfalls being numerous and, if fallen into, fatal to the production of trustworthy results. For the zonal relationships are not only less prominently brought into notice during the use of the two-circle method, but are even frequently obscured.

An interesting and important example of this is afforded in the work of one of the ablest and most accurate observers by the two-circle method, A. S. Eakle, whose excellent research on colemanite has been quoted earlier in this chapter. In a subsequent memoir<sup>1</sup> to the one describing colemanite Eakle described the crystals of a borate from Los Angeles County of California, of similar chemical composition and physical characters to colemanite, but which he concluded was different in its crystallographic and optical characters; while also of monoclinic symmetry it appeared to possess a totally different arrangement of faces and forms, and he considered it a separate new mineral, to which he gave the name "neocolemanite."

In a communication made in 1912 to the Mineralogical Society<sup>2</sup> Dr. A. Hutchinson showed that Eakle's two-circle measurements were capable of a different interpretation, and that by a change in the orientation of the crystals of neocolemanite they could be brought into complete harmony with those of colemanite. Hutchinson gives a stereographic projection of colemanite, as measured both by Jackson and by Eakle, and then also one for neocolemanite as described by Eakle, the symmetry plane being the plane of projection in each case. Hutchinson then shows that if a copy of the neocolemanite projection be made on tracing-paper and then this paper be reversed, back to front, and applied to the colemanite projection so that the primitive circles are coincident and the pole of the face (001) of the one lies exactly over that of the other, the two entire projections, and therefore the crystallographic characters of the two substances, are found to be absolutely identical. The directions of the optic axial planes of the two supposedly different minerals also then become coincident. Thus "neocolemanite" was in reality colemanite. The identity had escaped Eakle entirely through the use of the two-circle method and the gnomonic projection. If the stereographic projection had been made use of, and more attention paid to zones, to their complete measurement on the single-circle goniometer, and to their interzonal relationships, such an error would have been impossible.

Hence an emphatic warning is obviously necessary against obsession with the two-circle method, which its votaries are somewhat prone to develop. It is excellent in its place, especially for rapid work, but it is not the most trustworthy method for the highest purposes of original research.

**V. Goldschmidt's Two-circle Contact Goniometer.**—The principle of the two-circle goniometer has been applied by V. Goldschmidt<sup>3</sup> in a

<sup>1</sup> *Univ. Calif. Publ. Bull. Dept. Geol.*, 1911, 6, 179.

<sup>2</sup> *Min. Mag.*, 1912, 16, 239.

<sup>3</sup> *Zeitschrift für Kristallographie*, 1896, 25, 321.

contact goniometer for the measurement of large crystals with dull faces, and for the demonstration of the two-circle method with large crystals and crystal models. It is shown in Fig. 390.

The horizontal circle *H* is divided directly into single degrees, and may be read to half a degree with the aid of an indicator *a*. This circle *H* rotates with the crystal *b*, which is attached by wax on the crystal-holder *c*, the latter being rigidly fixed in the top of the crystal-adjusting movement by the screw *d*, the square head of which is manipulated by the lower end of the key *e* shown to the right. The upper end of the key is for insertion into two holes *f* and *g*, at right angles to each other, in the head of the crystal-adjusting movement *h*. The latter is a universal ball-and-socket joint, sunk in the upper part of the main central supporting column *k*. The vertical

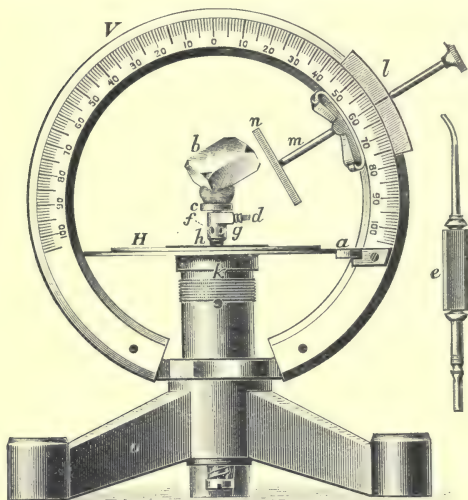


FIG. 390.—Goldschmidt's Two-circle Contact Goniometer.

circle *V* is of hoop form, and is graduated for 100° right and left of the zero at the top of the vertical diameter. An indicator *l* is maintained in close contact with the limb by a spring, and it carries a radial rod *m* terminating in the perpendicular contact-plane *n*; the rod can be pushed further in towards the centre, or withdrawn therefrom, in order to approach or recede from the crystal face parallel to which it is desired to adjust the contact-plane; the rod is maintained throughout strictly radial by means of springs. The apparatus is mounted on a stout tripod *o*. In another form of the apparatus the contact-plane disc is replaced by a long wedge, the edge of which is adjusted parallel to the crystal face instead of the plane surface of the disc.

In using the instrument the crystal is usually set up on the holder *c* with the prism zone, if one be prominently developed, vertical, perpendicular to the horizontal circle *H*; or, what comes to the same thing, if the crystal be tabular parallel to the basal plane, it is adjusted so that the latter face is parallel to *H*. The contact-plane *n* is then arranged with its rod vertical and the indicator at 0°, or horizontal with the indicator at 90°, and the basal plane or prism face is adjusted truly parallel to the contact-plane disc *n* by "sighting"; that is, by approaching the surface of *n* to the crystal face until it is nearly in contact with the latter, and then adjusting the crystal, by manipulation of the ball-and-socket joint with the key, until when regarded from all sides against a suitable background an equally thick or thin line of light is seen between the two surfaces. A circular background of white, black, or coloured cardboard, according to the colour or appearance of the crystal (that one being selected which offers the greatest contrast), may be attached just below the crystal, being gripped between *c* and *h*, the stem of the crystal-

holder passing through a central hole in the card. When the crystal is neither prismatic nor tabular, but more or less spherical, the ordinary method of the two-circle goniometer is followed, two faces being adjusted to the contact-plane in succession, both circles being employed. It is to be remembered, however, that the functions of the two circles are the opposite of what they are in the reflecting two-circle goniometer of V. Goldschmidt, for instead of the adjustment of reflections the adjustment to parallelism of the traces of the face and contact-plane is substituted. The reading  $v$  on the horizontal circle  $H$  gives the azimuth  $\phi = v - v_0$ , where  $v_0$  is the reading for the selected first meridian. The reading on the vertical circle  $V$  gives the polar distance  $\rho$  immediately.

**V. Goldschmidt's Apparatus for the Construction of Crystal Models.**—V. Goldschmidt<sup>1</sup> has further utilised the principle of the two-circle goniometer in an apparatus for the accurate construction of crystal models. It is shown in Fig. 391 in the improved form in which it was described in

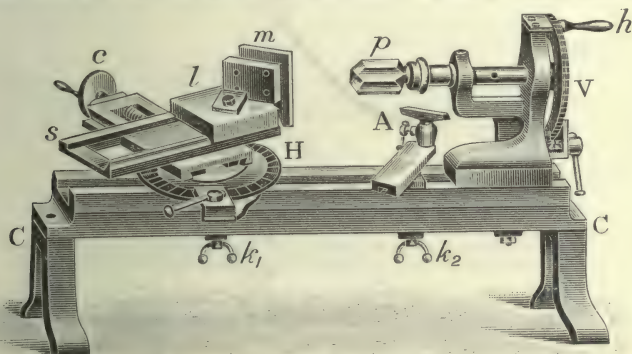


FIG. 391.—V. Goldschmidt's Crystal-Model-making Apparatus.

the year 1908. By the kindness of Miss Porter of Oxford, the author is also enabled to add Fig. 391a, prepared from a photograph by the makers, showing the apparatus in its latest form as constructed in the year 1920, by the successor, F. Rheinheimer, of P. Stoë, Heidelberg, by whom the earlier Goldschmidt instruments, including the two-circle goniometer, were made. It consists of three parts, carried on a kind of lathe bed ( $C$ ). The first is a vertical circle  $V$ , the axis of which carries the piece of modelling material  $p$ , which may conveniently be freshly prepared plaster of Paris (still moist), steatite, wax, or solid paraffin; this is supported by a relatively large crystal-holder or working piece, at the end of the horizontal axis of the vertical circle  $V$  (the  $\phi$ -circle in this apparatus). The second is the horizontal circle  $H$  ( $\rho$ -circle), which is massively constructed as a rotatable working table, and carries the vertical cutter  $m$ , which resembles the blade of a carpenter's plane; the support  $l$  for the latter is arranged to slide in a suitable guiding bed  $s$  in the plane of the face which it is desired to prepare on the crystal model. The planing thus occurs by the

<sup>1</sup> *Zeitschrift für Kristallographie*, 1899, 31, 223; 1908, 45, 573.



rapidly repeated sliding of the plane up and down in the bed *s*, slice after slice being planed away until the face is sufficiently developed. The screw movement *c* affords the necessary centring adjustment, for arranging the distance of the face from the centre of the model. A scale is provided adjoining the drumhead to record the complete turns of the screw, so that the distance of the face from the centre of the model can be as finely regulated as desired, in order to give the crystal model the habit contemplated. The whole planing gear and the circle *H* carrying it can be adjusted so as to approach the model or to recede away from it at will, and it can be fixed in the desired position by means of the screw clamp *k*<sub>1</sub>. The third part is an adjustable rest *A* for any other cutting tool or polisher which it may be desired to employ, and it can be fixed in the desired position by the clamping screw *k*<sub>2</sub>. The two circles *V* and *H* are divided to single degrees, and with the aid of an indicator the tenths of degrees can be estimated.

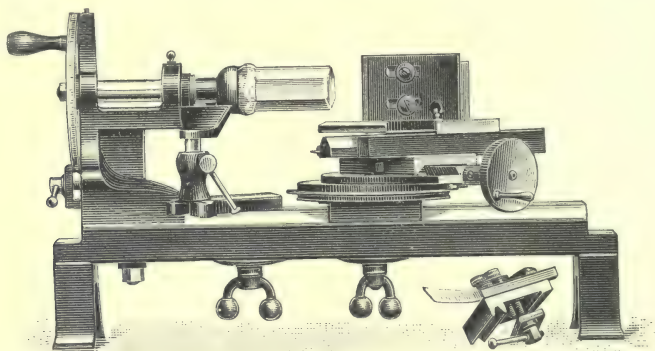


FIG. 391a.—Latest form of Goldschmidt Crystal-Model-making Machine.

In using the apparatus, the larger habit-conferring faces are first prepared, each of these dominating faces being produced in turn by the removal of successive shavings of plaster of Paris or paraffin, or whatever other material is being employed, the two circles being adjusted in accordance with the known values of  $\phi$  and  $\rho$  for each particular face. When the ideal development of these primary faces is desired, the planing tool is worked in each case until the drum and scale record the same reading.

The earlier form of the instrument, described in the first edition of this book, was more or less limited in its direct usefulness to the construction of the faces at one end of the crystal axis, which is arranged parallel to the axis of the vertical circle *V*. The other parallel faces had to be prepared with a second setting subsequently, or by simply preparing them with the aid of calipers in the ordinary way. In the later forms shown in Figs. 391 and 391a the faces at the other end of the crystal can also be cut. The re-entrant angles of twin-crystals can also be modelled. The central distances can be regulated to within half a millimetre. Provided

adequate care be taken to set accurately the angular values of  $\phi$  and  $\rho$  on the two circles, and the position of the planing tool to the proper central distance, the models furnished transcend in accuracy anything previously attempted. The instrument also serves as an accurate contact goniometer for the measurement of the angles between the faces of models, or between those of real crystals of considerable size. A special crystal-holder is provided, specially suitable for use on these occasions.

**Stöber's Contact Theodolite Goniometer and Crystal-Model Cutter.**—The stoutly constructed instrument shown in Fig. 392 has also recently been devised by F. Stöber<sup>1</sup> for the same purposes as Goldschmidt's apparatus.

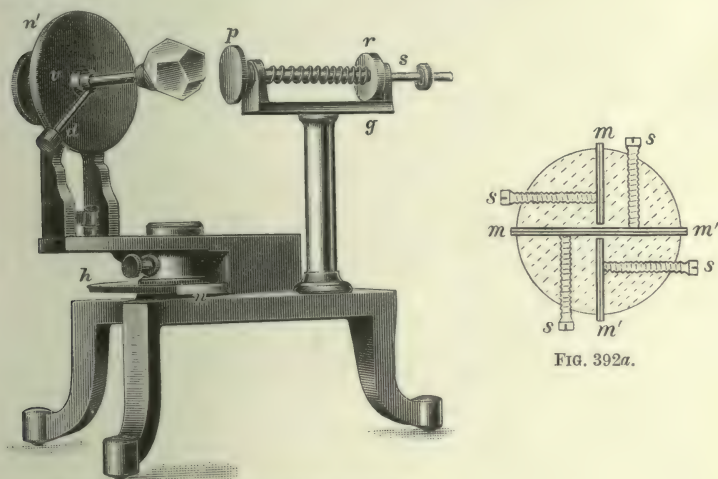


FIG. 392.—Stöber's Crystal-Model Maker.

In the vertical axis of a solidly built tripod a horizontal circle  $h$  is rotatable, and provided with a vernier  $n$ . The vertical circle  $v$  with its vernier  $n'$  is erected upon it by means of an elbow-piece, which is rotatable along with the horizontal circle about the same vertical axis as the latter. Both circles are provided with fixing screws, and the two verniers enable circle readings to be made to  $5'$ . The large crystal to be measured by contact is mounted at the end of a steel axis carried by the vertical circle  $v$ , and can be fixed by the screw  $d$ . On one of the feet, which projects somewhat more than the other two, the fork  $g$  is supported by means of a stout pillar. It carries a horizontal slider  $s$  at the height of the axis of the circle  $v$ . The slider may be pushed forwards towards the crystal, against the pressure of a spiral spring, and carries the contact plane  $p$  at its end nearest the crystal.

When the instrument is to be used for the cutting of a crystal model, the contact plane  $p$  is replaced by a cutting plane shown separately on the right in Fig. 392a. It consists of a bronze plate carrying

<sup>1</sup> *Zeitschrift für Krystallographie*, 1914, 54, 283.

crosswise two razor edges of hard steel  $mm'$ , which are fixed by the setting screws  $ss$ . The cutting plane is rotated by means of a driving band passing over the pulley  $r$ , and worked to and fro (up and down) by the

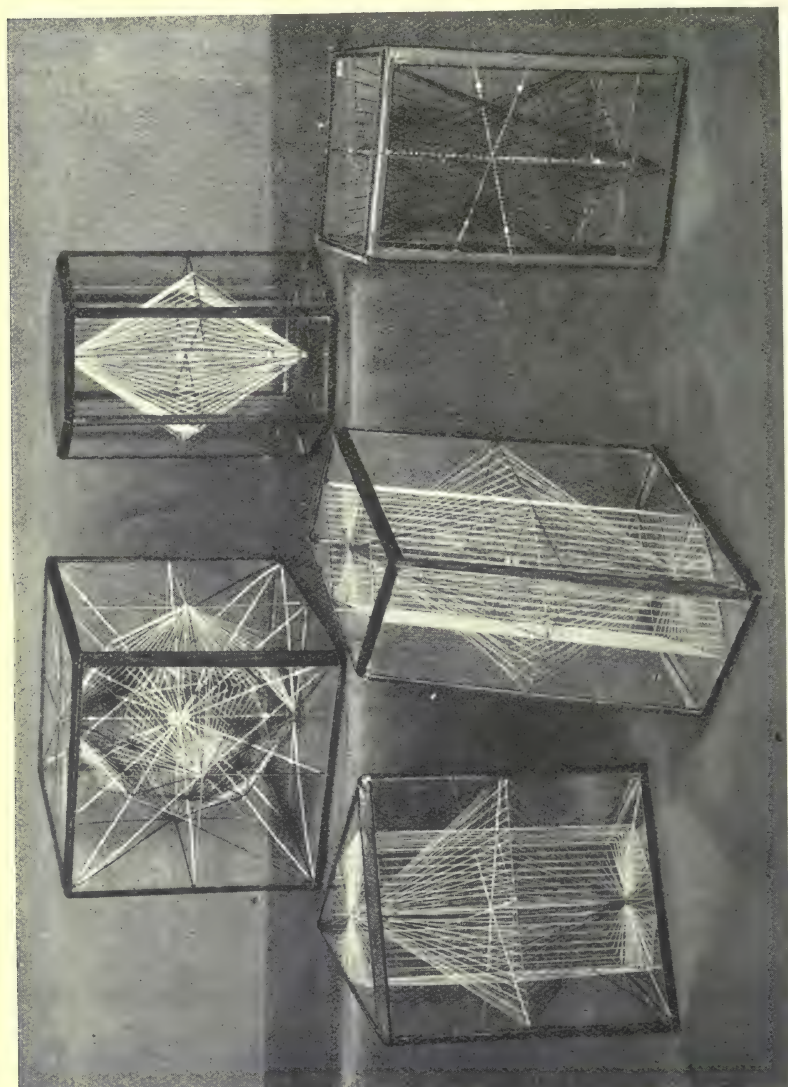


FIG. 393.—Crystal Models constructed by Miss Hosali.

two hands, or presumably more conveniently by means of any suitable whirling table or electric motor. The block to be planed into a crystal model is fixed on the steel axis of the circle  $v$ , instead of a crystal, a hole two centimetres deep being first bored into the block and the axle end



fixed in the hole with suitable cement, such as Canada balsam, sealing wax, or seccotine. The model material must not be too hard, plaster of Paris mixed with 20 per cent of calcium silicate or China clay, kneaded with water and pressed into a block, being very suitable, cutting readily and taking sharp edges. A model 6-7 centimetres in diameter, fairly rich in faces, can be readily made within an hour, after a little practice.

**Models of Crystals.**—Excellent models of crystals, in boxwood, glass, or plaster of Paris, both simple forms and combinations such as are exhibited by many naturally occurring substances, are supplied by the chief mineralogical firms. It is often of great assistance in a crystallographic investigation to be in possession of a good set of models, and still better to be able to cut a model for oneself at any moment with the aid of either of the two instruments just described. The elucidation of a difficult problem of symmetry, twinning, or other complexity is frequently materially aided by having recourse to a model.

Probably the most beautiful and instructive models of crystals yet produced are those which have been made by Miss Nina Hosali, and exhibited and described to the Mineralogical Society on November 7, 1916; they were subsequently exhibited at the Royal Institution and at the meeting of the British Association at Bournemouth in 1919. A set of these exquisite models has been made by Miss Hosali for the author, and the accompanying Fig. 393 shows five of them, those for classes 32, 25, 22, 14, and 2. Two or more forms are represented in each model, by means of coloured silk threads, each form in a separate colour, and they are enclosed in a glass envelope, the shape of which corresponds to another form of the same crystal class. For convenience, cubes in the cubic system, and prisms in the other systems, have been chosen as the most suitable forms for the envelopes. The crystallographic axes, the planes of symmetry, centres of symmetry, and axes of symmetry, are all very clearly indicated by threads or wires of different thickness and colour, so as to render each morphological or symmetry element quite distinctive. Moreover, the degree of symmetry of each of the symmetry axes is also clearly indicated by a minute neat label. These models are not merely very beautiful works of art, but are calculated to be of the greatest possible use as aids to the study of difficult cases of symmetry. The great advantage of being able to see right through the crystal, owing to the openwork of the thread-structure of the planes, and thus to trace all the various axes and planes right through the crystal substance, will at once be obvious. The models reveal the inner structure of the crystal, as regards its crystallographic and symmetry elements, in a more perfect and complete manner than the author has ever previously seen attempted.



PART II

CRYSTAL STRUCTURE AND ITS X-RAY  
ANALYSIS





## CHAPTER XXVIII

### COMPOSITE CRYSTALS AND TWINNING

THE perfectly formed single crystals required for the purpose of goniometrical measurement are, as will have been abundantly clear from the earlier chapters of Part I. of this book, by no means invariably easy to obtain. The vast majority of natural mineral crystals, and a considerable number of those grown artificially from solution, exhibit some form of aggregation. After having completed the accurate description of the crystallographic symmetry and its elements, and determined the interfacial angles, with the aid of single crystals of the highest attainable degree of perfection, it is both interesting and important to include in the scope of the investigation a description of such mode or modes of aggregation as are found to be characteristic of the substance. For it is a fact that usually one or two very definite types of composite crystal are found to be peculiar to a particular mineral or to a specific chemical preparation.

There are three main kinds of composite crystal, namely: (1) parallel growths, (2) twin crystals, and (3) aggregates which are neither twins nor completely parallel growths, but which are arranged so that one particular edge or face of each individual, the prism edge or the basal plane for instance, is always arranged parallel to the corresponding edge or face of each of its neighbours. Completely parallel growths and twins are much the more common occurrences, however, when the crystals have been allowed to grow free from disturbance. The study of these composite crystals, especially of parallel growths, is so intimately connected with that of the internal structure of crystals, that it has been considered best to include this chapter in Part II. of the book, which deals with Crystal Structure.

**Parallel Growths.**—In a parallel growth of different individuals of the same substance all the corresponding edges and faces of the various individuals are parallel, supposing all of them to show the same forms. An excellent example is potash alum, the well-known double sulphate of potassium and aluminium which crystallises with 24 molecules of water of crystallisation,  $K_2Al_2(SO_4)_4 \cdot 24H_2O$ ,<sup>1</sup> or almost any of the salts isomorphous with it, all known as alums whatever the second metal may be.

<sup>1</sup> Considered constitutionally; the empirical (half) formula  $KAl(SO_4)_2 \cdot 12H_2O$  is also much used.

The cubic octahedra of the alums are often formed in columnar piles of parallel crystals, as shown in Fig. 394; the planes of contact are parallel to the cube-face (001), and the centres of successive octahedra, indicated by the dots, lie in the prolongation of the vertical axis. It will be obvious that rotation for  $90^\circ$  or  $180^\circ$  of any one or more of the octahedra effects no change in the aspect of the pile. If the same forms be not present, the parallelism consists of a parallel arrangement with respect to the crystallographic axes.

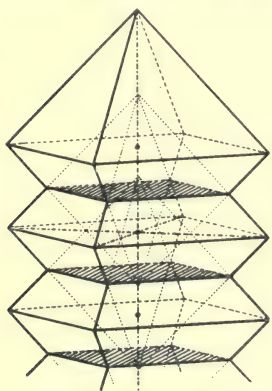


FIG. 394.—Parallel Growths of Alum.

Such parallel-growth aggregates usually reveal themselves by the fact that all the parallel faces become illuminated at the same time by parallel rays of light, so that simultaneous reflections are obtained from them. This is well seen on the goniometer when the crystals are sufficiently small, and the signal-images simultaneously reflected from the individual parallel facets ought, of course, to coincide into an identical image. Such composite crystals, however, are rarely sufficiently perfect for this to happen, and usually a bundle of images is afforded, lying the closer together the greater the degree of perfection. These parallel growths of the **same** substance do not call for any further structural study, for they would never be selected for goniometrical work, except to verify the fact that the substance has a tendency to produce such parallel growths.

The subject of the conditions under which parallel growths of one substance can be formed on the crystals of **another** has been investigated by Barker,<sup>1</sup> who has shown from experiments with a large number of salts that only those substances which possess similar molecular volumes and molecular distance (topic axial) ratios (discussed in Chapter XXXI.) exhibit the property of forming such parallel growths. It is doubtless due to the congruency, close similarity, all but identity, of the space-lattice structure, that is, the like symmetry and very near equality of the absolute dimensions of the structural-unit parallelepipeda of the

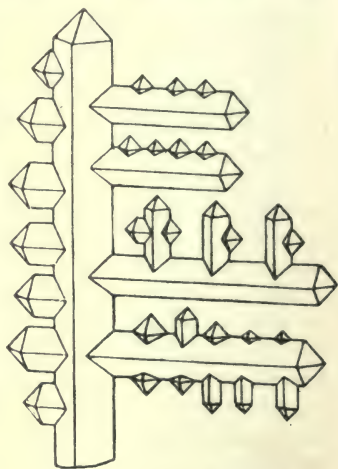


FIG. 395.—Parallel Growths of Native Copper.

<sup>1</sup> *Journ. Chem. Soc.*, 1906, 89, 1120; *Mineralog. Mag.*, 1907, 14, 235.



space-lattices, in these cases, that parallel growths of the two crystal substances are capable of formation one on the other. One of the most interesting cases is that of the parallel-growth crystals of sodium nitrate,  $\text{NaNO}_3$ , which form very readily on calcite,  $\text{CaCO}_3$ , in the manner illustrated (by kind permission of Mr. Barker) in the beautiful photograph reproduced in Fig. 396. Although these two substances are not isomorphous in the usually accepted sense, yet they are almost perfectly isostructural, possessing similar rhombohedral symmetry and almost identical molecular volumes and topic axial ratios; that is, the shape, volume, and edge dimensions of their structural-unit cells are practically identical.

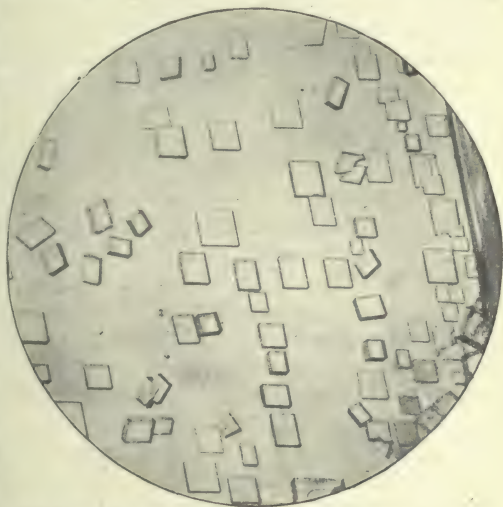


FIG. 396.—Parallel Growths of Sodium Nitrate on Calcite.

The parallel growths formed by the members of isomorphous series one on another form a most important study. Their relative facility of formation is proportional to their nearness in molecular volume and topic axial ratios. Thus in the case of the rhombic sulphates of potassium, rubidium, caesium, and ammonium, the extreme members, potassium and caesium sulphates, exhibit no tendency to the formation of either parallel growths or mixed crystals, their molecular volumes and topic axial ratios being considerably different; while the potassium and rubidium (or ammonium) salts, and the caesium and rubidium (or ammonium) salts, for which the volumes and cell-unit dimensions are closer, exhibit a distinct but not great tendency to form parallel or overgrowths and mixed crystals. On the other hand, the rubidium and ammonium salts, which possess remarkably close (almost identical) molecular volumes and topic axial ratios, crystallise together in mixed crystals or as overgrowths or parallel growths with the utmost readiness. These facts, and many similar ones observed by Barker, have been confirmed and extended by Wulff<sup>1</sup> and by the author.<sup>2</sup> The latter has shown that the remarkable isostructure of the rubidium and ammonium salts is also exhibited in the case of the selenates and throughout the whole extensive series of monoclinic double sulphates and selenates containing  $6\text{H}_2\text{O}$ , isomorphous with the ammonium magnesium sulphate so fully worked out in Chapter XVII.; and that this isostructure is invariably accompanied by ready facility for the growth of mixed crystals, parallel growths, zonal growths, and complete overgrowths.

<sup>1</sup> *Zeitschr. für Kryst. Min.*, 1906, 42, 558.

<sup>2</sup> *Roy. Soc. Proc.*, 1917, 93, 75.

**Twin Crystals.**—Crystals are frequently found which are obviously of a composite character, that is, are composed of more than a single individual crystal of the same substance, and in which the two or possibly even three parts, clearly belonging to different individuals, are united in a definite and regular manner, other than parallelism, the particular mode of union being characteristic of the substance. The twin nature is often betrayed by the presence of “re-entrant angles,” forming notches, arrow-head shapes, knee-shapes, cruciform, or heart shapes; but not infrequently the two or more individuals are so intimately blended that the appearance at first sight is that of a single individual crystal, and possibly of that of a crystal of a higher degree of symmetry than the single crystals of the particular substance have been already proved to exhibit.

The “twin law” defining the manner in which composition occurs is usually stated in terms such as the following: The two individuals are first supposed to be arranged parallel to each other, with one face of each in mutual contact, and then in order to produce the twin one individual is supposed to be rotated for  $180^\circ$  upon a plane, which is usually although not necessarily the contact face, called the “twin plane,” and about the normal to this plane as axis, which is termed the “twin axis.” Sometimes, as just suggested, the common plane of symmetry is not the face of contact, and it is then distinguished as the plane of “composition.” In general, the plane of twinning may be any actual or possible face of a form developed or possible on the crystal, except obviously a plane of symmetry, and usually it is one with low indices, and indeed very often a primary face.

But this mode of stating the nature of the regular mode of composition of twins is misleading, as it is based on or bound up with the idea of rotation of one individual with respect to the other, whereas the twin is simply the expression of the fact that the growth of the crystal has occurred simultaneously according to two distinct but intimately related orientations, owing to the molecules of the substance in the act of crystallisation taking up two alternative positions with equal facility. If stated as above, the idea that one individual has been actually joined to the other after an actual rotation for a semicircle is somehow involuntarily and erroneously conveyed.

A much preferable mode of stating it is that **a twin crystal consists of two individuals united symmetrically about a plane, the “twin plane,” which is not one of systematic symmetry but a possible face of the crystals of the substance, or about an axis, the “twin axis,” which is a possible crystal edge.** Besides being a mode of expressing the rule less liable to misinterpretation, it is also a more accurate statement; for all twins cannot be explained on the theory of rotation through a semicircle.

In the case of “juxtaposition twins” the plane of union, whether the twin plane or not, is known as the “plane of composition.” “Interpenetration twins,” however, have no plane of composition. Hence, **the only true elements of twinning are the twin plane and the twin axis.** The effect of complete interpenetration twinning without re-entrant angles is often apparently to convert a crystal belonging to a class lower



than the holohedral into a holohedral crystal of the same system of symmetry. This type of twinning is, therefore, termed "supplementary."

There are well-known twins formed by the union of enantiomorphous crystals, that is, of a right-handed variety with a left-handed one, and which belong to a class of symmetry possessing neither a plane nor a centre of symmetry; these cannot be described at all as obtained by rotation, for no amount of rotation can bring a truly enantiomorphous crystal into coincidence or parallelism with its oppositely enantiomorphous fellow. Such twins are best described as "mirror-image" or "reflection twins," for one individual is symmetrical to the other about the plane of reflection, although the twin cannot be explained by rotation about this plane, so that the plane of twinning is not a rotation plane in such a case. An excellent instance is afforded by the famous twins of Brazilian quartz, shortly to be described.

Hence, it must now be clear that we have **twins characterised by possessing a twin plane, which is a possible face of the crystal and is a plane of symmetry of the twin but not of the single crystal, and which may have a twin axis normal to it; also other twins endowed with a twin-axis only, which is a possible edge of the crystal; and others again which may be ascribed to reflection across a plane, which is a possible facial plane.** If the two supplementary individuals belong to a class of their system lower than the holohedral, and the twin plane or plane of reflection is a symmetry plane of the holohedral class, or if they are twinned about a twin axis which happens to be an axis of symmetry in the holohedral class, the resulting solid will exhibit the exterior symmetry of the holohedral class, and the more indistinguishably from a truly holohedral crystal the more complete the interpenetration of these supplementary twins.

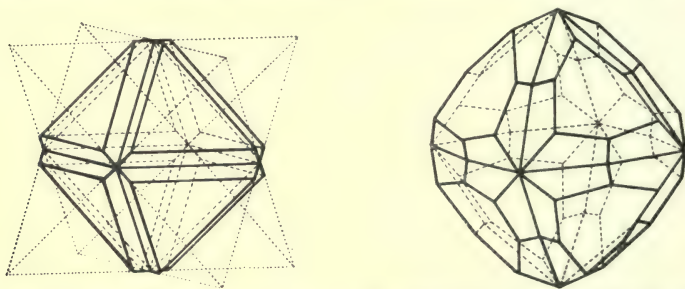
It will be obvious from the foregoing that no general rule applies to the phenomenon of twinning, and that it is, therefore, incumbent to describe each variety of twin, of every specific crystallised substance, on its own merits. No investigation of a new substance is complete without the description of all the varieties of twinning which the substance is observed to exhibit. As the main purpose of this book is to give instructions for practical work, a few typical examples will now be given of well-known twins of the different varieties which have been referred to, selected from all the systems of symmetry, and these will be followed by the description of a few twins met with in the course of the author's own investigations, which will best elucidate the mode of tackling the investigation of the twins of a new substance. A description will then be given, in conclusion, of the principles underlying the drawing of twin crystals, with one or two specific examples from recent investigations.

The "**notched**" or **grooved type of twin** is very well shown by the diamond, a complementary pair of positive and negative tetrahedra, or of hexakis tetrahedra, twinned about a cube face, interpenetrating to produce an apparent octahedron or hexakis octahedron, but with more or less deep grooves along the octahedral edges, owing to the interpenetration not being absolutely complete.



Two such diamonds are represented at (a) and (b) in Fig. 397.

There is considerable doubt, however, as to whether this proves the diamond to belong to the hexakis-tetrahedral class of the cubic system (class 31), for not only have hexakis octahedra of diamond been found,



(a) Twinned Tetrahedra of Diamond.

(b) Twinned Hexakis Tetrahedra of Diamond.

FIG. 397.—Two Characteristic Twinned Diamonds.

showing no trace of grooving, but also the cleavage is truly octahedral, and no proof of electric polarity has ever been brought forward, or of any kind of polarity of the trigonal axes of symmetry, all indicating that there is a possibility that the diamond may really belong to the holohedral class 32 after all. Indeed definite evidence has been adduced of the absence of electric polarity in a memoir by van der Veen,<sup>1</sup> who decides for holohedral symmetry. Moreover, the results of the X-ray analysis of the structure of the diamond by Sir William Bragg and Prof. W. L. Bragg appear to have conclusively proved its holohedral character (see Chapter XXXIII.). There is no doubt, however, as to the frequent occurrence of twin tetrahedra and hexakis tetrahedra, of the type shown in the figures, and also a few simple tetrahedra have been from time to time discovered.

The notched appearance is also typical of the well-known rhombohedral twins of calcite, twinned on the basal pinakoid (111). Precisely similar twins are also exhibited by an organic substance already mentioned in Chapter VI., methyl triphenylpyrrholone. This substance has been shown by the author to be dimorphous, having both a triclinic form and a trigonal one. The triclinic variety is illustrated in Figs. 47 and 48 (page 98), being used as a particularly typical example of a triclinic substance. The trigonal variety belongs to the calcite class, and a single crystal of rhombohedral habit is shown in Fig. 398, the chief forms being the basal pinakoid  $c=\{111\}$  and the primary positive rhombohedron  $r=\{100\}$ , the complementary negative rhombohedron  $r'=\{22\bar{1}\}$  being very subsidiary. Fig. 399 shows a characteristic twin, resembling one of calcite, composed of a pair of positive rhombohedra  $r=\{100\}$  twinned upon the basal pinakoid  $c=\{111\}$ , as plane of both twinning and composition, re-entrant angles being shown at the three equatorial corners.

**The arrow-head appearance** is very characteristic of twins of gypsum

<sup>1</sup> *Kon. Akad. Amsterdam*, 1907, p. 182.

(selenite)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Fig. 400 represents a single crystal of gypsum of a very common type, and Fig. 401 an arrow-headed twin formed by the union of two such individuals. The twin plane and plane of composition is the ortho-pinakoid (100), neither of the two faces of which form is developed on the commoner crystals. The twin may best be described as a reflection twin about the ortho-pinakoid as the mirror, but it may also be said to be produced by rotation of one of a pair of originally parallel crystals for  $180^\circ$  about the normal to (100) as twin axis.

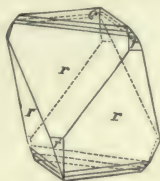


FIG. 398.—Rhombohedral Crystal of Methyl Triphenylpyrrolone.

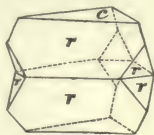


FIG. 399.—Twin of Methyl Triphenylpyrrolone.

**Elbow- or knee-shaped twins** are particularly characteristic of

tinstone (cassiterite),  $\text{SnO}_2$ , and of rutile, one of the two tetragonal forms of titanium dioxide,  $\text{TiO}_2$  (anatase described in Chapter XIII. being the other). A characteristic twin of tinstone, in which the twin plane is a face of the form  $\{101\}$ , is represented in Fig. 402, the indices of the front faces being given, in order to assist in rendering clear the derivation of the lower individual. A triplet of rutile, the twin plane of which is also a face of  $\{101\}$ —sometimes given as (011), the complementary plane of equal value to (101) as regards the symmetry—is also shown in Fig. 403. The forms present are the

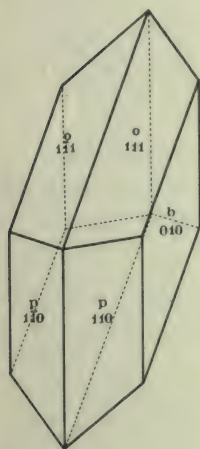


FIG. 400.—Crystal of Gypsum.

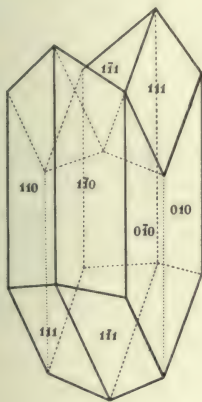


FIG. 401.—Twin of Gypsum.

prism  $p = \{310\}$  and the primary bipyramid of the first order  $o = \{111\}$ . The central individual shows no faces of the latter form, and the prism faces are simply marked with the form letter  $p$ . To indicate that the faces showing in front of the upper and lower individuals would be back faces if twinning had not occurred, the form letters  $p$  and  $o$  are distinguished from those of the middle individual by a negative sign. Rutile is an excellent example of multiple twinning, for not only, as in this case, is a third individual added to an ordinary twin, but often the repeated or so-called "polysynthetic" twinning is continued several times, and in some remarkable rutile crystals from Georgia eight individuals are twinned one after another on different faces of the same form  $\{101\}$ , giving rise to a complete ring. They do not lie in the same plane, however, but are inclined  $65^\circ 35'$  to one another in a zigzag.

The cruciform shape is exhibited characteristically by the rhombic

mineral staurolite, an aluminium iron silicate, and a typical instance is shown in Fig. 404, in which the twin plane is a face of the possible brachy-prism  $\{032\}$ , while the only faces actually shown on the crystals themselves are those of the basal pinakoid  $\{001\}$ , brachy-pinakoid  $\{010\}$ , and the primary rhombic prism  $\{110\}$ . The indices of the front faces

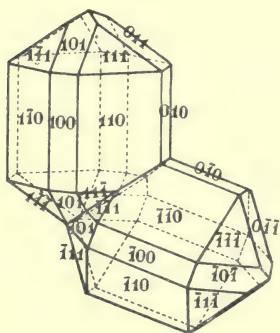


FIG. 402.—Twin of Cassiterite.

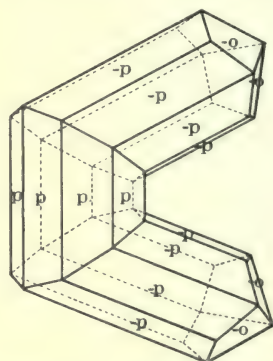


FIG. 403.—Triplet of Rutile.

of both individuals are marked in the drawing, those of the second or transverse one corresponding to the back faces of the first or vertical one, which latter is arranged in the normal position of a single crystal.

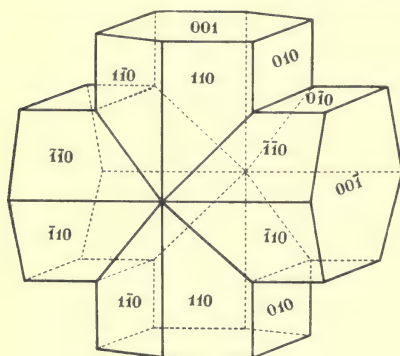


FIG. 404.—Twin of Staurolite.

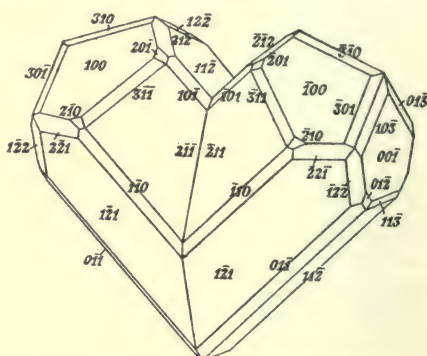


FIG. 405.—Twin Crystal of Calcite from Egremont.

**Of heart-shaped twins** an excellent example is afforded by the double crystal of calcite from Egremont, Cumberland, shown in Fig. 405, which is reproduced, with the author's kind concurrence, from a memoir by Dr. Stefan Kreutz on calcite twins contributed to the *Denkschriften der kaiserlichen Akademie der Wissenschaften* (math.-naturw. Klasse, vol. 80), Vienna, in the year 1906. The twin plane is a face of the primary rhombohedron  $\{100\}$ .

It will have been observed that **interpenetration** occurs in the case of staurolite, the two individuals passing completely through each other



and reappearing on the other side. A similar kind of interpenetration occurs in the well-known case of fluor-spar, fluoride of calcium  $\text{CaF}_2$ , in which two cubes, twinned on an octahedron face (111) as twin plane, or about the common cube diagonal as twin axis, interpenetrate and project beyond each other in the manner shown in Fig. 406.

Another case of considerable importance is that of the two complementary pentagonal dodecahedra of pyrites  $\text{FeS}_2$ , {210} and {120},

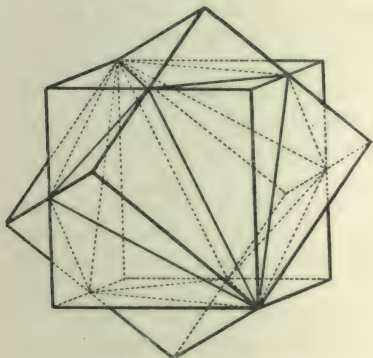


FIG. 406.—Twin of Fluor-spar.

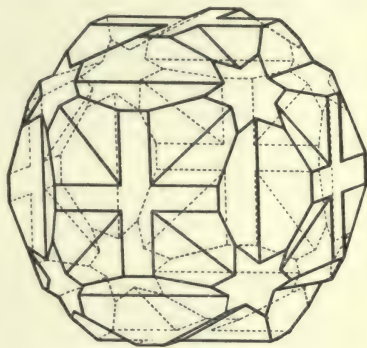


FIG. 407.—Twin of Pyrites.

twinned (reflected) about a face of the rhombic dodecahedron {110}, and interpenetrating and passing beyond one another in the manner indicated by the re-entrant angles in Fig. 407, which represents one of the beautiful twins from Minden in Prussia. A cross is formed by the long edges of the two different pentagonal dodecahedra, parallel to each cube face, the centre of the cross being at each axis-end; and in the example shown in the figure the sharp crossed edges are actually blunted by the faces of the cube, rendering the cross still more marked, and justifying the popular appellation conferred on these twins of “Zwillinge des eisernen Kreuzes.” The star-shaped faces at the diagonal corners are octahedron faces replacing common corners of the two pentagonal dodecahedra.

When interpenetration of such complementary pentagonal dodecahedra is complete without the passage of either individual beyond the other, the solid produced is a perfect tetrakis hexahedron, indistinguishable as regards its exterior shape from the holohedral form. Hence, this is an excellent instance of **supplementary twinning**, where two individuals belonging to a class of symmetry lower than the holohedral combine to produce the holohedral form of the same system. The two diamonds shown in Fig. 397, composed of two interpenetrating tetrahedra and hexakis tetrahedra respectively, are also supplementary twins, and when the interpenetration is just complete without any sign of grooves the solid is either the octahedron or the hexakis octahedron, indistinguishable in appearance from those two holohedral solids of the cubic system. Diamonds are actually found in which this is the case, the octahedron being, however, the commoner, and although very frequently the faces are curved, many diamonds have been found which

are perfectly sharp and plane-faced octahedra. In the case of pyrites there is no doubt whatever that the true class is the pyrites class 30, and not the holohedral class 32 of the cubic system. But in the case of the diamond, the question has already been said to be less clear, and it may be that while the commoner habit is that of the hexakis-tetrahedral class 31, the truly holohedral habit occasionally occurs, and that the diamond really possesses full holohedral class-32 symmetry. In this event a supplementary twin would be hard indeed to distinguish from a holohedral diamond, and the very fact of there being this interesting discussion over the diamond is of itself eloquent testimony to the close simulation of holohedral symmetry which supplementary twinning may evoke, and therefore to the need for a very sharp look-out to be kept, when investigating the crystals of a new substance, for the least sign of twinning.

There is a further case introducing the phenomenon of enantiomorphism which ought to be referred to, as the mineral has been taken in Chapter XXIII. as an example of trigonal symmetry, and forms an especially good instance of an enantiomorphous substance, namely, that of quartz. Figs. 311 and 312 (page 355) in Chapter XXII. illustrate the two kinds of quartz crystals, Fig. 312 the right-handed and Fig. 311 the left-handed. Fig. 408 represents a twin quartz crystal, in which two right-handed crystals are intergrown in accordance with a plan which may be described as equivalent to rotation for  $180^\circ$  about the vertical axis, and so completely without projection beyond each other that the crystal is apparently a single one. But it will be observed that the little faces of the right trigonal pyramid  $s$  and of the right trapezohedron  $x$  are present on two adjacent corners ( $60^\circ$  removed) of the crystal, whereas a truly single crystal shows them only on alternate corners. Moreover, in ordinary single quartz crystals the faces of the rhombohedron  $r = \{100\}$  are usually bright, and those of the inverse rhombohedron  $r' = \{2\bar{2}1\}$  dull; but in this twin crystal one part of each rhombohedron face is generally bright and the rest dull, the two parts being more or less irregular and corresponding to the two different individuals. These two individuals are related to each other as if, starting with the pair parallel (both right-handed as in the case chosen for Fig. 408, or both left-handed), one of them had been rotated round the vertical axis for  $180^\circ$ , bringing the direct or positive rhombohedron of the one parallel to the inverse or negative rhombohedron of the other. Such twins of either right-handed or left-handed quartz are fairly common, and the amount of interpenetration varies from only very partial, showing re-entrant angles, to complete as shown in Fig. 408.

Quartz, however, exhibits yet another kind of interpenetration twin, as already mentioned, which is characteristic of crystals from Brazil. Two differently enantiomorphous individuals, that is, a right-handed and a left-handed, are here combined, and when the interpenetration is but partial, as in Fig. 409, the twin has the appearance of a mirror-image or reflection twin. But when the interpenetration is complete, the two rhombohedra coincide and the little  $s$ - and  $x$ -faces occupy symmetrical

positions, as shown in Fig. 410. The symmetry is obviously with respect to vertical planes passing through the centre of each parallel pair of prism faces, so that the twinning may be described as upon a face of the second order prism  $\{10\bar{1}\}$ . The rhombohedral faces of the two interpenetrating individuals being coincident, the direct of one with the direct of the other individual, and the inverse of the one with the inverse of the other, there are no irregular patches of dull and bright natural

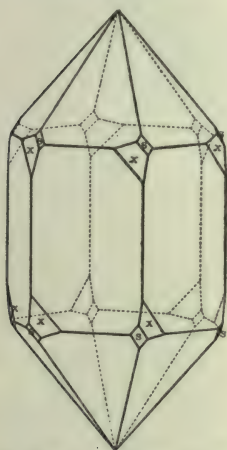


FIG. 408.—Interpenetration Twin of Right-handed Quartz.

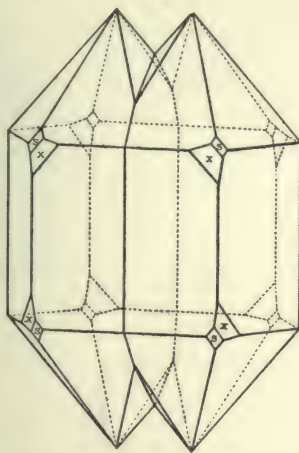


FIG. 409.—Partial Interpenetration Twin of Right- and Left-handed Brazilian Quartz.

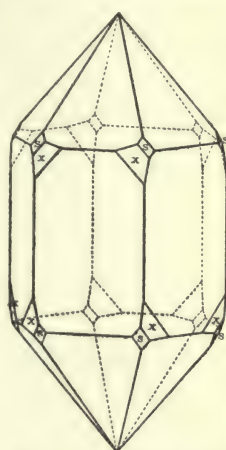


FIG. 410.—Complete Interpenetration Twin of Brazilian Quartz.

polish exhibited, as in the case of the other variety of quartz twin shown in Fig. 408.

**Repeated Twinning.**—One case of repeated twinning has already been described in the triplet of rutile (Fig. 403), but the repetition is by no means confined to the formation of triplets, or even of rings of seven or eight individuals; it may occur any number of times. Carried to the extreme, this phenomenon gives rise to one of the greatest difficulties which may confront the crystallographer, for a crystal built up of innumerable twin lamellæ is not at all uncommon, and if the fact be not detected the failure leads to an erroneously high estimation of the symmetry; for the latter is lower than the apparently single crystal would appear from its exterior shape to possess. It will subsequently be shown that the optical properties exhibited by such a composite crystal are also anomalous, and often most difficult to unravel, for the individual laminæ are occasionally not merely microscopic in thickness but actually ultra-microscopic. But the very fact that the optical characters are not normal is a warning to look out for possible repeated twinning.

An excellent example is afforded by the triclinic (holohedral) soda feldspar albite,  $\text{NaAlSi}_3\text{O}_8$ . A characteristic twin of this mineral is shown in Fig. 411, the twin plane being the brachy-pinakoid  $b=(010)$ . The two long upper  $c$ -faces show a re-entrant angle, and are the two different



basal pinakoid faces ( $001$ ) and ( $00\bar{1}$ ) of the two individuals; the two front  $p$ -faces are the prism faces ( $110$ ) and ( $1\bar{1}0$ ), and the two  $r$ -faces are ( $10\bar{1}$ ) and ( $\bar{1}01$ ). The twinning on this plan, however, may be so often repeated that a crystal having the shape of a single crystal as in Fig. 412 is produced, composed of innumerable alternate lamellæ of the two kinds

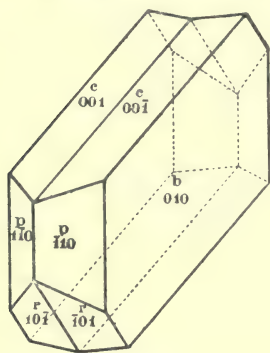


FIG. 411.

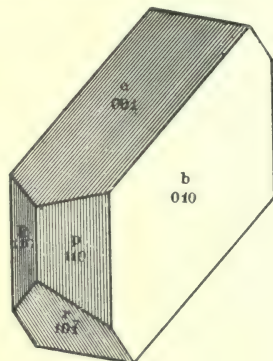


FIG. 412.

of individual, the only exterior sign of which is the striation indicated by the shading lines in the figure. A section-plate of such a crystal, cut transversely to the twinning, would exhibit differently coloured strips under the polarising microscope, corresponding to, and indicating clearly, the different individuals. But it can readily be imagined that a section parallel to the plane of twinning, and thick enough to include quite a number of separate individuals, would either show no indication of twinning at all or would present some anomalous phenomenon in polarised light. If the layers having the direction of one crystal individual predominate in thickness, the alternating reversed individuals being much thinner, the apparently single crystal resulting is of triclinic habit, more or less resembling a single crystal of albite, as drawn in Fig. 412. But if the layers average equal thickness, the habit becomes pseudo-monoclinic, the upper and lower edges becoming more or less parallel to the normal to  $b = \{010\}$ , although they are seen to be serrated when examined with a lens. Such a crystal then resembles very closely the monoclinic crystals of the corresponding potash felspar, orthoclase,  $\text{KAlSi}_3\text{O}_8$ . Indeed the most recent research has indicated the possibility that orthoclase itself may be really triclinic, but so extremely finely and evenly twinned in innumerable repetitions that the microscope is incapable of detecting the separate individuals. A second variety of potash felspar, microcline, is distinctly triclinic, and shows visible multiple twinning, thus lending considerable support to this view.

A remarkably beautiful case of repeated twinning is that of right- and left-handed quartz in amethyst. The repetition of alternations of the two varieties is so frequent, the laminae so thin, that the external appearance of a single crystal is afforded, and it is only on cutting a section-plate, preferably 2-4 millimetres thick, and examining it in polarised

light, so as to take advantage of the opposite rotations of the plane of polarisation by the two varieties, that the structure is revealed, although the part which shows the lamination is frequently of a pinkish purple colour in ordinary light, that currently described as "amethyst." This violet-coloured portion is often arranged in alternate  $60^\circ$ -sectors of the section, as shown on Plate III. in Fig. 413, which represents, in its natural size, a magnificent section-plate 9 mm. thick cut from a fine amethystine quartz crystal, perpendicular to the axis. The violet staining of the alternate sectors appears very deep, and these sectors reveal even to the naked eye the lamination, on close scrutiny. The lamination is parallel to the edges of the second order hexagonal prism and perpendicular to those of the first order prism forming the boundary of the section, and thus, when viewed in polarised light, often appears parallel to lines radiating from the centre and inclined at  $120^\circ$  or as a series of hexagons one within another, repeated many times in alternate light and dark or coloured lines from the centre to the edges of the section, as shown in Fig. 414 on Plate III., or even more frequently as a combination of both, the former occupying the central portion. The more regular varieties showing striæ parallel to lines radiating at  $120^\circ$  from the centre usually exhibit this phenomenon only in the central part, passing as the hexagonal edges of the section are approached into uniform regions of right- or left-handed quartz brilliantly polarising in even colours. A very beautiful section of such an amethyst, nearly 2 inches in diameter, as seen in parallel polarised light, is shown in Fig. 415 on Plate III. In the dark field of the lantern projection polariscope the laminae, as seen on the screen, show not only alternate bright and dark strips, but the dark lines themselves are alternately very black and less dark. When the analysing Nicol is rotated the lamination is exhibited in the most beautiful variety of colours and neutral tints. The blacker lines seen when the Nicols are crossed are black extinction bands, due to the section-plate being oblique to the plane of the lamination, which is apparently parallel to the rhombohedral planes of gliding with which quartz has been shown by J. W. Judd<sup>1</sup> to be endowed; so that two successive laminae overlap, and one being right-handed and the other left-handed, and producing equal and opposite retardation<sup>2</sup> in the central line of the overlapping portion, a black extinction band, that of the dark field of the crossed Nicols, is here produced. This intimate repetition twinning consequently causes the crystal to exhibit an apparently non-rotatory character in the part where such lamination occurs, and to show in convergent polarised light the usual black cross and circular rings of an ordinary uniaxial crystal of an optically inactive substance. The marginal part where a region of right- or left-handed quartz is found shows both rotation and the special uniaxial figure of either right or left quartz, rings without black cross in the central part of the field (see Fig. 801, in Chapter L.),

<sup>1</sup> *Mineralog. Mag.*, 1892, 10, 123.

<sup>2</sup> The laminae being oblique to the section-plate, which is cut perpendicular to the optic axis, the phenomena of double refraction as well as those of optical rotation enter into the case.

and at the junction of two such marginal regions of opposite rotations the overlapping strip shows Airy's spirals (Fig. 802), as usual for a single overlapping of the two varieties of quartz.

This will be rendered clearer by the plan, given by Professor Judd and reproduced in Fig. 416, of an amethyst very similar to that belonging to the

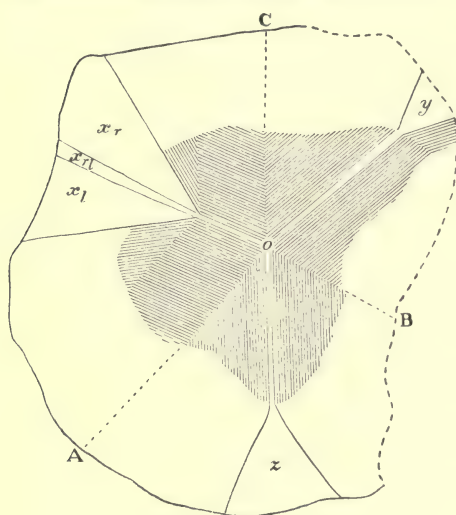


FIG. 416.—Structure of Amethyst.

author shown in Fig. 415. The wedge-shaped portions marked *y* and *z* are respectively composed of left-handed and right-handed quartz, both showing even tints in parallel polarised light. The larger wedge *x* is composite, the part *x<sub>r</sub>* being right-handed and *x<sub>l</sub>* left-handed. The surface of junction of the two parts is not perpendicular to the plate, so that the overlapping part *x<sub>rl</sub>* shows a ribbon band in parallel polarised light, and Airy's spirals in convergent polarised light. The remaining sectors, divided by the lines A, B, C, show no trace of circular polarisation owing to intimate lamellar twinning, and the central

part, where the lamellæ are very well developed and are exhibited very plainly in parallel polarised light, affords the ordinary uniaxial interference figure of rectangular cross and circular rings.

An extreme case of repeated twinning is exhibited by crystals of potassium chlorate,  $\text{KClO}_3$ . Lord Rayleigh has shown that many crystals of this salt are composed of multiple twins of practically equal thickness. R. W. Wood<sup>1</sup> has described a crystal of chlorate of potash, a thin flake, in which there were 700 laminæ, each only one five-thousandth of a millimetre thick. What is most remarkable, however, is that the laminæ are of constant thickness in any one and the same crystal, while the thickness varies in different crystals of the same lamellar constitution. It appears as if a crystal which starts with an alternation of a pair of plates of a specific thickness maintains this same repetition-constant throughout the growth of the whole structure. A most remarkable play of colour, first described by Sir George Stokes, is exhibited by these crystals of potassium chlorate in casually reflected light. Sir William Crookes possessed a very beautiful collection of such apparently brilliantly coloured crystals of chlorate of potash, the colours changing with the position of the observer. In one of his last papers Lord Rayleigh<sup>2</sup> gave a detailed mathematical analysis of reflection from such regular stratification, when the number of alternations is very great, and showed that the phenomenon was susceptible of a very precise explanation on the lines

<sup>1</sup> *Phil. Mag.*, 1909, 18, 535.

<sup>2</sup> *Roy. Soc. Proc.*, 1917, 93, 565.





FIG. 413.—Section-Plate of Amethyst Quartz, natural size, showing alternat  
Violet Sectors in Ordinary Light.

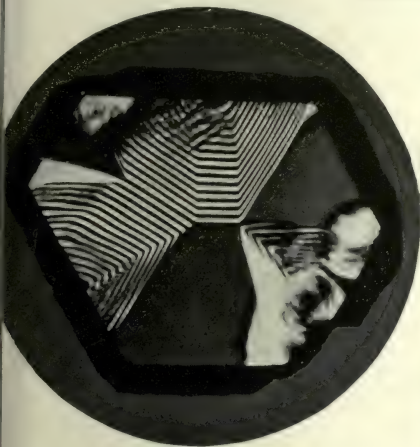


FIG. 414.—Section-Plate of Amethyst Quartz, show-  
ing sectorial repeated Twinning of Right and  
Left Varieties, in parallel Polarised Light.

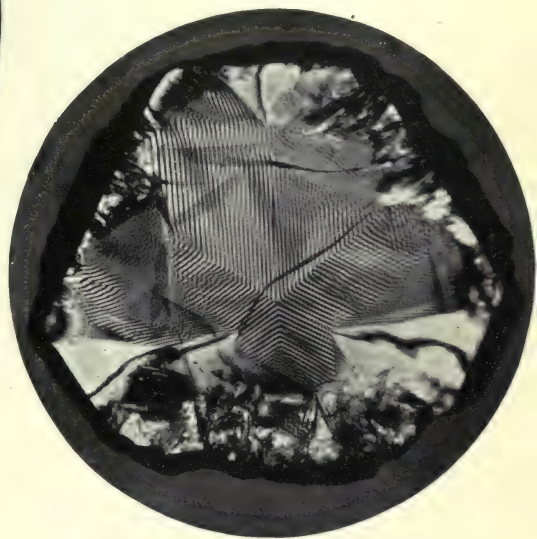


FIG. 415.—Section-Plate of Amethyst Quartz, showing  
relatively large Area of repeated Twinning of Right-  
and Left-handed Quartz, in parallel Polarised Light.

AMETHYST QUARTZ IN ORDINARY AND POLARISED LIGHT.

*Plate to face page 510.*



indicated above. By transmitted light the crystal appears quite colourless and single.

The author has often been struck with the regularity in the thickness of the laminae exhibited by amethyst, in a very fine collection of amethyst sections which he possesses for projection purposes. Some of these amethysts, such as that illustrated in Fig. 415, afford simply gorgeous effects on the screen in parallel polarised light, especially as the analysing Nicol prism is rotated, and which are of a highly instructive character as regards the structure of the crystals.

**Mimicry of Higher Symmetry brought about by Twinning.**—We have already seen in several cases of supplementary twinning that a twin pair of individuals belonging to a class of symmetry lower than the highest (holohedral) which the system is capable of exhibiting may simulate the holohedral class of that system. Occasionally this simulation goes higher still, to another and higher system altogether. An approach to this has just been referred to in the case of a triclinic feldspar becoming apparently monoclinic. One of the best known, however, of these cases of “mimetic twinning,” and a perfectly definite one, is that of the rhombic salt so often referred to in this book, as typifying many of the most interesting properties of crystals, potassium sulphate,  $K_2SO_4$ . It has already been shown in an earlier chapter that the prism angles between the respective two pinakoids  $a=\{100\}$  and  $b=\{010\}$  and the two prisms  $p=\{110\}$  and  $p'=\{130\}$  are very nearly  $30^\circ$  and  $60^\circ$ , and this is true for the whole series of alkali sulphates and for the isomorphous selenates. In the case of potassium sulphate the actual angles are:  $ap=29^\circ 48'$ ,  $pp'=30^\circ 0'$ , and  $p'b=30^\circ 12'$ . Thus, to begin with, the prismatic zone of a single crystal is only  $12'$  from being truly hexagonal; and as the principal terminal faces are those of (1) the primary bipyramid  $o=\{111\}$  corresponding to the primary prism  $p=\{110\}$ , and (2) the brachy-domal prism  $q'=\{021\}$  corresponding to the brachy-pinakoid  $b=\{010\}$  and having the same intercept on the vertical axis as the pyramid  $o=\{111\}$ , it will be obvious that if the faces  $b$ ,  $p$ ,  $o$ , and  $q'$  are developed in anything like equipoise a solid closely resembling a hexagonal prism doubly terminated by the bipyramid will be produced. The prism, moreover, may be shortened until the appearance is that of a simple hexagonal bipyramid. An intermediate case, when the prism and brachy-pinakoid faces still clearly show around the equatorial base of the bipyramid, is shown in Fig. 417, which represents an actual crystal of rubidium sulphate,  $Rb_2SO_4$ , the second member of the family series of alkali sulphates; but the habit is equally applicable to potassium sulphate, although it is not so common in the case of this first member of the series.

The remarkable thing is, however, that these salts, and most especially potassium sulphate, have a pronounced tendency to form triplets, which resemble hexagonal bipyramids even more closely than do these occasionally occurring pseudo-hexagonal single crystals. The author possesses a large number of excellent triplet-bipyramids of potassium sulphate, and one of them is faithfully represented in Fig. 418.



The striking likeness to Fig. 417 is quite remarkable. But on close inspection of the two crystals the faces of that shown in Fig. 417 are observed to be truly plane and in every way goniometrically excellent, as should be the case with a perfect single crystal; whereas the crystal portrayed in Fig. 418 exhibits a very low linear ridge down each face, as indicated by the shading; it is not always or even generally symmetrically placed, but sometimes nearer the polar pyramidal edge on the one side and sometimes nearer that on the other; the face obviously consists of two parts, one of which is not truly parallel to the other, the two behaving in fact like vicinal faces. The goniometrical positions of the two portions are only a few minutes apart, but the line of demarcation between them is quite distinct, and is almost a sure sign either of twinning or of the presence of vicinal faces.

As a matter of fact, these ridges are due to the crystal being a triplet, the three individuals interpenetrating according to a plan which will be rendered clear by Fig. 419, which is an orthometric projection,

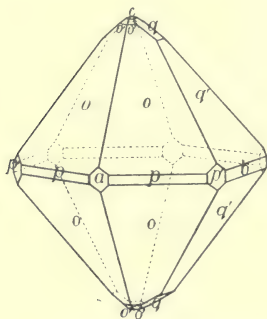


FIG. 417.—Crystal of Rubidium Sulphate.

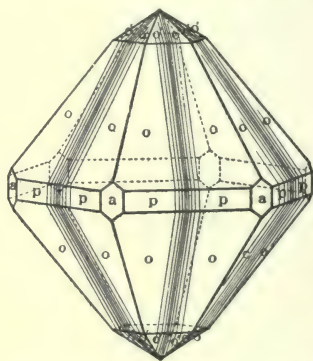


FIG. 418.—Triplet of Potassium Sulphate.

that is, a geometric plan from directly above the crystal, projected on the equatorial plane. The circumferential edges all represent in plan the faces of the primary prism  $p = \{110\}$  and of the macro-pinakoid  $a = \{100\}$ ; and the continuous radii indicate the polar edges between the primary bipyramid faces  $o = \{111\}$ . The dotted radii represent the dividing lines between the separate crystals, and the two parts of each one of the three individuals are shaded with parallel lines. The angle  $ap$  being  $29^\circ 48'$ , the angle  $pp$  at the corner where the little  $a$ -face truncates it is twice this,  $59^\circ 36'$ . There are six of these angles on the triplet, but they together only make up  $357^\circ 36'$ , so that if the twin plane were precisely perpendicular to  $p = (110)$ , and the  $p$ -faces of two individuals after twinning were exactly congruent and in the same plane, there would be a gap of  $2^\circ 24'$  at the finish. But the plane of twinning must be regarded as not precisely perpendicular to  $p = (110)$ , but differing therefrom by one-twelfth of the discrepancy just mentioned, namely, by  $12'$ , the difference of  $ap$  from exactly  $30^\circ$ ; for the solid is completed without a gap. That is, the twinning occurs as if the crystal were truly and not

merely pseudo-hexagonal. But every pair of adjacent  $p$ -faces belonging to two different individuals are consequently not in precisely the same plane, the normal to one part making an angle of  $24'$  with the normal to the other part. This accounts for the ridge, and for the fact that one half of the face reflects light at a different moment from the other half on the other side of the ridge. No gap is ever apparent if no faces of the other prismatic form  $p'=\{130\}$  are present. If  $p'$ -faces are present, however, little re-entrant angles are found, as indicated in the second orthometric projection in Fig. 420. These, however, are not gaps, but

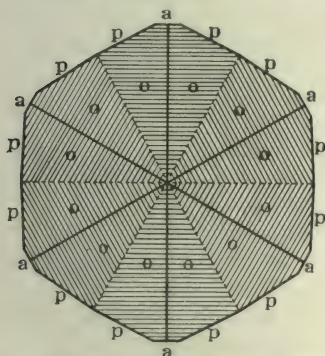
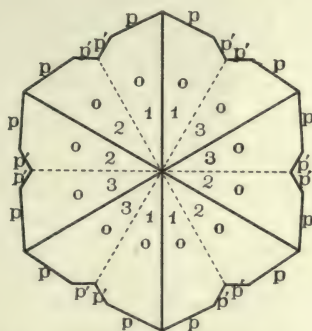


FIG. 419.—Plan of Triplet of Potassium Sulphate.



true re-entrant angles. They are visible on several of the crystals of potassium sulphate in the author's collection. These faces of  $p'=\{130\}$  are nearly parallel to the planes of twinning of the three individuals, as the angle  $pp'$  is  $30^\circ 0'$ . In Fig. 420 the three individuals are numbered, so that the parts belonging to the same individual, expressed by similar shading in Fig. 419, may be readily recognised.

It will be clear from the foregoing what an excellent instance of mimetic repeated twinning potassium sulphate forms. The presence of the ridges, and the duplicate images  $24'$  apart given by the prism faces, and corresponding vicinal-face phenomena also exhibited by the two parts of each of the pyramid faces, would put an experienced crystallographer on his guard against assuming that the crystal was a simple hexagonal one. The biaxial optical properties, moreover, would render any such erroneous supposition impossible, and would establish the fact that although the habit was pseudo-hexagonal, the system of symmetry was really rhombic.

Fig. 421 gives an example of a similar triplet of the isomorphous potassium selenate,  $K_2SeO_4$ , the composite crystal being an elongated pseudo-hexagonal prism terminated by the two pseudo-hexagonal pyramids; the construction is exceedingly like that of potassium sulphate, but the angle  $pp$  is  $59^\circ 38'$  instead of  $59^\circ 36'$ , the difference of the twin plane from perpendicularity to  $p=(110)$  is  $11'$  instead of  $12'$ , and the angle across the little ridge in the middle of the  $p$ -faces is  $22'$  instead of  $24'$ .

A very instructive further triplet of potassium selenate is also shown in Fig. 422, which is very characteristic of this salt. The interpenetration is less complete, none of the three individuals passing right through the structure so as to be continued on the other side, so that the horizontal section of the composite crystal is a three-rayed star. Re-entrant angles are formed by the brachy-pinakoid *b*-faces and the brachy-domal *q* and *q'*-faces.

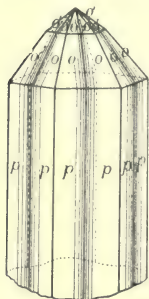


FIG. 421.—Triplet of Potassium Selenate. Complete Interpenetration.

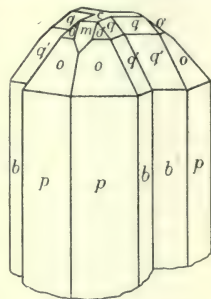


FIG. 422.—Triplet of Potassium Selenate. Incomplete Interpenetration.

**Practical Mode of dealing with Twins.**—In the investigation of a new crystalline substance careful watch must be kept for any signs of twinning among the crystals of the numerous crops prepared, and after the completion of the goniometry proper, carried out upon the

best single crystals, such twins as have been found should be thoroughly examined, and measured if such a course be necessary to elucidate the plan on which the twinning is accomplished. For the kind or kinds of twin, or of still higher polysynthetic structure, which may be developed by a substance in the act of crystallisation, forms an essentially characteristic property of the substance. The chief object, of course, is to discover the exact position of the plane or axis of twinning, and to ascertain the typical mode in which the composition occurs, that is, whether by interpenetration, juxtaposition, or both. Perhaps the best mode of illustrating the *modus operandi* of this part of the investigation will be to take a concrete example from the author's own experience.

**Example of Investigation of a Twin.**—The case chosen, a typical and not too simple one, is that of ammonium selenate,  $(\text{NH}_4)_2\text{SeO}_4$ , the investigation of which was published in the year 1906.<sup>1</sup>

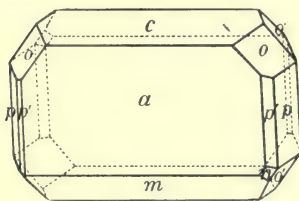


FIG. 423.—Monoclinic Crystal of Ammonium Selenate.

This salt is dimorphous, having a rhombic form isomorphous with ammonium and potassium sulphates and the rest of the alkali sulphates and selenates, and a monoclinic form. The former is only known in mixed crystals with ammonium sulphate, potassium selenate, or best of all with rubidium selenate, which last-mentioned salt mixes in the solid crystalline state with the greatest facility with ammonium selenate on account of the closeness of their molecular volumes and molecular distance (topic axial) ratios (relative distances apart of the molecular or polymolecular centres along the crystallographic axes), in accordance with the rule as to isostructure of ammonium and rubidium salts referred to under "parallel growths" earlier in this chapter. The ammonium selenate crystals obtained in the usual way from a solution

<sup>1</sup> *Journ. Chem. Soc.*, 1906, 89, 1066.



in water of the pure salt are invariably those of the monoclinic variety. A characteristic crystal is shown in Fig. 423, and its stereographic projection is shown in Fig. 42 on page 86.

The habit is prismatic along the symmetry axis  $b$ . The ortho-zone parallel to this axis shows the faces of  $c = \{001\}$ ,  $a = \{100\}$ , and  $m = \{20\bar{1}\}$ , so that three different angles are observed to occur, each in duplicate as two parallel faces constitute each of the three forms. These angles are:

$$ac = (100) : (001) = 64^\circ 31'; \quad cm = (001) : (\bar{2}01) = 68^\circ 22'; \quad ma = (\bar{2}01) : (\bar{1}00) = 47^\circ 7'.$$

Now in the twins this zone, in many cases indistinguishable at a cursory glance from that of a single crystal, shows only two of these angles,  $64^\circ 31'$  and  $68^\circ 22'$ , each in duplicate, the third angle being altogether absent; its two values of  $47^\circ 7'$  are replaced, one in each semicircle, by the two different values  $50^\circ 58'$  and  $43^\circ 16'$ . It was discovered that  $50^\circ 58'$  was afforded by two adjacent  $a$ -faces, and  $43^\circ 16'$  by a pair of adjacent  $m$ -faces, the sequence of angles in the zone being:

$$\begin{aligned} ca &= 64^\circ 31' \\ aa &= 50^\circ 58' \\ ac &= 64^\circ 31' \\ cm &= 68^\circ 22' \\ mm &= 43^\circ 16' \\ mc &= 68^\circ 22' \end{aligned}$$

On some of these twins the edges  $aa$  and  $mm$  were not sharp, but were grooved along their entire length with a re-entrant angle formed by two narrow strips of  $m$  or  $a$ -faces respectively, which gave quite trustworthy images of the signal-slit, so that there was no doubt about the nature of the faces. A section of such a prism is shown in Fig. 424 which will render the construction quite clear.

It will be obvious that we are dealing with a twin, the re-entrant angles being conclusive, and that the plane of twinning is parallel to the basal pinakoid  $c = (001)$ , the twin axis being normal to that face. The angles are marked in the drawing, and it will be evident from them how the two twin angles  $aa$  and  $mm$  come to be  $50^\circ 58'$  and  $43^\circ 16'$ , as observed.

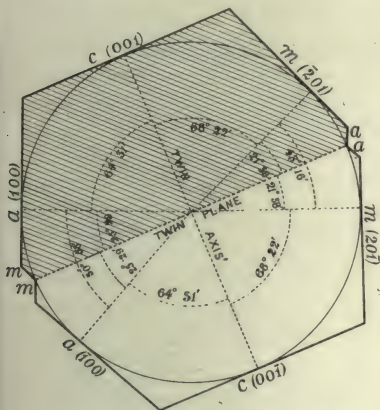


FIG. 424.—Section of Ortho-zone of Ammonium Selenate Twin.

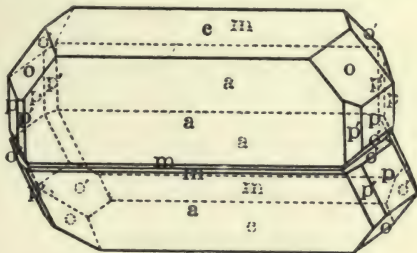


FIG. 425.—Twin of Ammonium Selenate.

Fig. 425 shows the appearance of one of these twins which had the grooves best developed, indeed that at the back was quite a wide re-entrant angle, the two  $a$ -faces forming it being quite broad; it will be apparent from the figure that the end-faces also exhibit re-entrant angles. The dotted letters in the figure refer to the back faces. The chief zone affected, involving end-faces, is  $[copo'c]$ . The angles of this zone in a single crystal are as follows, each being repeated in the same order in the second semicircle:

$$\left\{ \begin{array}{l} co = (001) : (111) = 43^\circ 53' \\ op = (111) : (110) = 33 \quad 33 \\ po' = (110) : (111) = 43 \quad 16 \\ o'c = (11\bar{1}) : (001) = 59 \quad 18 \end{array} \right.$$

There are obviously two of these zones, the one the zone symbol of which has just been given and the complementary one [ $co'poc$ ], corresponding to the two zonal arcs terminating at  $c$ -poles shown on the projection in Fig. 42. But in a twin each of these two zones shows at one end instead of a single  $p$ -face two  $p$ -faces inclined at an angle of  $25^\circ 8'$ , and at the other end also two  $p$ -faces instead of one, but in a re-entrant angle, and the angle between the two  $o'$ -faces which are now brought on either side of the re-entrant angle (instead of one  $o$  and one  $o'$ -face of the single crystal) is  $61^\circ 24'$ . The two angles  $25^\circ 8'$  are in front, one at each end, and the two of  $61^\circ 24'$  behind. Further, a little groove-like re-entrant angle is also sometimes present between the two  $p$ -faces at each end which make the angle of  $25^\circ 8'$ , as shown in front in Fig. 425, due to two strips of  $o'$ -faces being developed, one on each individual. The two angles just quoted,  $25^\circ 8'$  and  $61^\circ 24'$ , were found by direct calculation to be exactly those demanded by a twin the plane of twinning of which is the basal pinakoid. The angle  $25^\circ 8'$  is clearly shown between the two front  $p$ -faces of the two individuals at the left end in Fig. 425.

The construction of this twin is therefore perfectly clear. The best idea of it is, of course, obtained from a model, and whenever any difficulty presents itself in the geometrical imagination of the solid, the author always has recourse to the cutting of a model out of cork, when the difficulty invariably disappears. It is best as a rule to cut out a duplicate pair of single-crystal models, and then to juxtapose them in the positions actually shown by the twin crystal, which is generally too small to be manipulated as a model can be; but in a case like the present, one model will probably suffice for most purposes, cut in two halves parallel to the basal pinakoid, the twin plane.

**The Drawing of Twin Crystals.**—The essence of the process of drawing a twin is the construction of a second axial system, at the correct position with respect to that of the ordinary single crystal. Each case should be dealt with directly from first principles, but there are a few helpful rules which may be given for the three possible cases, which are (1) when two of the three axes remain the same and only the third has a different direction in the second individual to what it has in the first; (2) when two axes have new directions in the second individual; and (3) when all three axes have entirely different directions in the two individuals.

(1) **When only One Axis has Different Directions in the Two Individuals.**—An excellent concrete example, which will admirably illustrate the mode of procedure, is afforded by the characteristic twin of monoclinic ammonium selenate represented in Fig. 425, and the character of which has just been fully described. The twin plane has been shown to be parallel to one of the axial planes, that containing the axes  $a$  and  $b$ , parallel to the basal pinakoid  $c = (001)$ . Hence, it is only a question of finding the new position of the axis  $c$  of the second individual, for the axes  $a$  and  $b$  are common to the two individuals. After having found the direction of this second axis  $c$ , the second individual can be drawn in the usual way about it and the two common axes, and at such a distance from the first individual as faithfully represents what is actually observed on a typical twin.

In finding the position of the  $c$ -axis of the second individual the following considerations and Fig. 426 will be helpful. If the strong lines  $aa$  and  $cc$  represent the axes  $a$  and  $c$  lying in the symmetry plane, which is taken as parallel to the plane





single crystal shown in Fig. 423. The second individual, the lower portion of the twin, is similar to the lower half of Fig. 423, but constructed about the new axis  $c$  inclined away to the back (and the same axes  $a$  and  $b$ ), and with such faces as were in front now inverted at the back. The proportions of the two individuals are such as were actually shown by the twin taken as the example, and the same applies to the dimensions of the narrow faces forming the grooves along the front and the front part of each of the two ends. To render everything absolutely clear, both the indices and the form letters are stated in Fig. 427, while in Fig. 425 the form letters for both front and back faces are given, those of the latter being dotted.

(2) When Two Axes have Different Directions in the Two Individuals.—Suppose

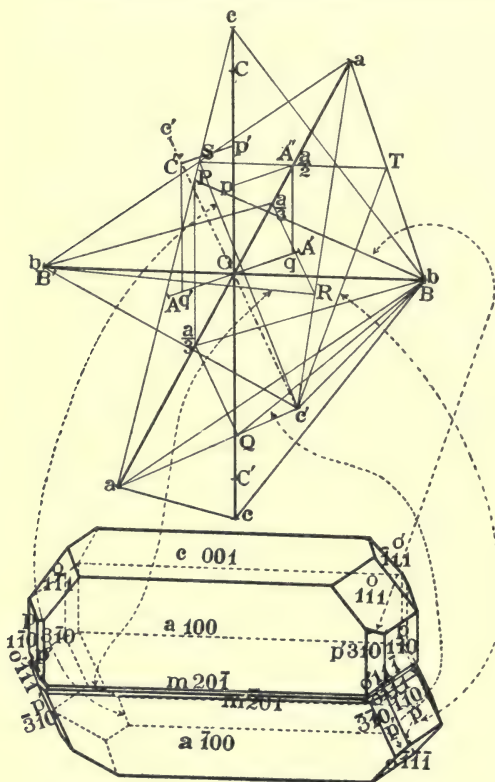


FIG. 427.—Construction of Axes and of Crystal-form of Ammonium Selenate Twin.

the axis  $b$  to be the one to remain unchanged in direction, as shown by the parallel lines  $BB'$  and  $BB'$  in Fig. 428. Suppose further that  $AA'$  and  $CC'$  are the  $a$  and  $c$ -axes of the first individual, and that the twin plane makes the intercepts  $C$  and  $A'$  on these axes, while parallel to the  $b$ -axis. We have to draw the new axes  $CC'$  and  $A'A'$  of the second individual at similar angles  $\theta$  and  $\phi$  on the other side of the twin plane  $A'C$ , as if by reflection across the latter; that is, we have to draw them so that the two angles marked  $\theta$  are the perspective representations of really equal angles, and the two marked  $\phi$  also similarly equal, in other words, the new  $c$ -axis is to be inclined  $(180^\circ - 2\theta)$  to the old  $c$ -axis, and the new  $a$ -axis  $(180^\circ - 2\phi)$  to the old  $a$ -axis. This we do in each case by a repetition of the same process as in case (1), that is, as for the construction of the inclined axis of a monoclinic crystal. Thus, for instance, at  $C$  we draw the cubic axes  $a$  and  $c$ , as shown dotted in Fig. 428, and we take along  $a$

in the backward direction the length  $a \cdot \sin(180^\circ - 2\theta)$  which is the same as  $a \cdot \sin 2\theta$ , and along the vertical axis  $c$  we take the length  $c \cdot \cos(180^\circ - 2\theta)$ . We then complete the parallelogram as usual, and join those two opposite corners of which  $C$  is one, and produce this diagonal for some distance backwards; this line  $CC'$  is then the direction of the new axis  $c$ . A similar process at  $A'$  using the angle  $\phi$  instead of  $\theta$  gives  $A'O'$ , the direction of the new axis  $a$ , and through the point of intersection  $O'$  of the two new axes  $a$  and  $c$  thus drawn the third axis  $b$  is drawn parallel to  $BB'$ . These three new axes  $a$ ,  $b$ , and  $c$  thus drawn are shown in Fig. 428 in broken-and-dotted lines to distinguish them from those of the first individual  $AA'$ ,  $BB'$ ,  $CC'$ . The proper length of the  $b$ -axis is afforded by drawing parallels to  $OO'$  through  $B$  and  $B'$ ,

meeting the new axis  $b$  at  $\bar{B}$  and  $\bar{B}'$ , which thus mark the unit lengths on each side of the centre  $O'$ . The upper and back halves of the new  $a$  and  $c$  axes are likewise made equal to the lower and front halves.

(3) When all Three Axes have Different Directions in the Two Individuals.—The procedure in this, the general, case consists of three operations.

We first draw in the usual manner the axial system for one of the two individuals, as if it were an ordinary single crystal.

Secondly, we draw the representation of the twin plane ( $hkl$ ), by joining its parametral points  $H, K, L$  on the axes thus drawn.

Thirdly, the axial system of the second individual is to be drawn, in such a manner that  $H, K, L$  are also the ends of the parameters of the twin plane with respect to these new axes, for the twin plane is common to the two individuals. Generally applicable rules for accomplishing this third operation are given in the following paragraphs labelled (a) to (f), and they are illustrated by a typical example the construction for which is worked out in Fig. 429.

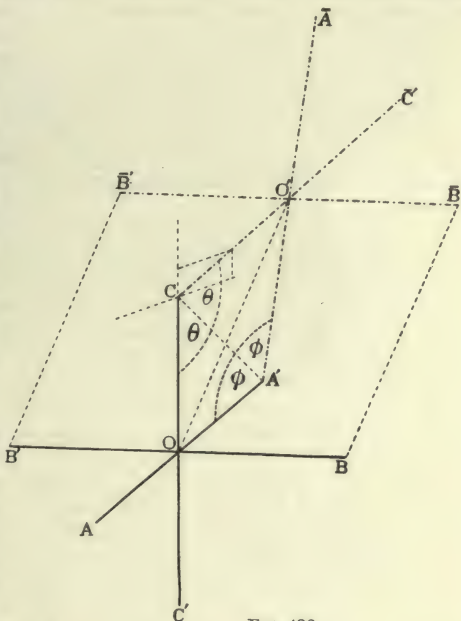


FIG. 428.

(a) We begin by finding the position of the twin axis with respect to the first, the ordinary, axial system, that is, we find the point (T in Fig. 429) at which the normal drawn from the centre  $O$  of the first axial system  $OA, OB, OC$  to the twin face (plane of twinning) meets that face.

The construction for finding this normal  $OT$  which the author finds most convenient is that recommended by Prof. von Groth. We first carry out the second operation of joining the parameters of the twin face on the three ordinary axes; in the example illus-

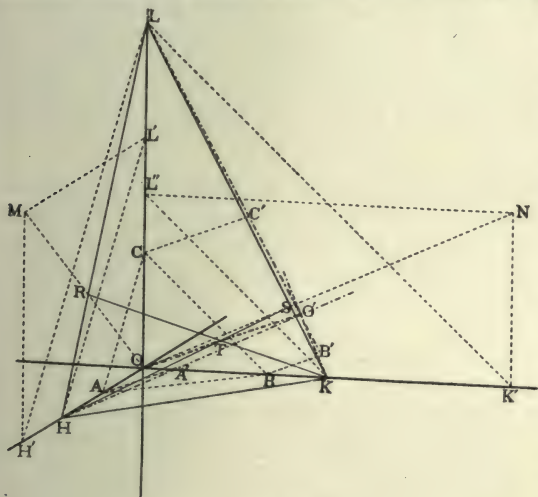


FIG. 429.

trated in Fig. 429 the points  $A, B$ , and  $C$  represent as usual the unit lengths, and the parameters of the twin plane are  $H, K, L$ , and are respectively in the case

chosen  $2a$ ,  $\frac{2}{3}b$ , and  $3c$ , that is, the twin plane HKL is the face (342), the plane ABC being (111).

We draw parallels to AC from H and L, meeting the axes  $c$  and  $a$  respectively at L' and H'; a similar pair of parallels to BC are next drawn from K and L, meeting axes  $c$  and  $b$  at L'' and K'. A pair of parallelograms are then completed by drawing parallels to OH and OL through L' and H', and to OK and OL through L'' and K'; and the two diagonals OM and ON are also drawn. These diagonals cut HL and KL, two of the continuous lines representing the twin plane, at R and S respectively; and by joining R to K and S to H we arrive at the desired point T where the normal to the twin plane from O meets that plane, for T is the point of intersection of RK and SH.

(b) The normal OT to the twin plane is produced to O' equidistant on the other side of the twin face, that is, so that  $O'T = OT$ . This point O' is the centre or origin of the new axial system of the second individual.

(c) The new axes themselves are at once given by joining O' to the parametral points H, K, L on the first system, as is done in broken-and-dotted lines in Fig. 429; for the plane HKL is common to the two systems of axes, and the same points must be the ends of the two sets of parameters.

(d) The primary parametral lengths A', B', C' of the second system are obtained by drawing lines to meet the new axes, from the parametral points A, B, C of (111) on the first system, parallel to the normal OO'.

(e) The face determined by A'B'C' will have opposite index signs to ABC, as the imaginary rotation for  $180^\circ$  will have brought it into the opposite octant. That is, faces appearing in the same (analogous) octant in the two individuals of the twin have opposite signs attached to their indices, as the second crystal is situated as if it had been rotated  $180^\circ$  with respect to the first crystal.

(f) The two individual crystals are to be drawn about their respective axial systems at such positions with respect to each other as best represent the observed facts on the actual twin crystal. The drawings of the two crystals can, of course, be transferred anywhere so long as they and their axes are moved parallel to themselves. In a perfectly interpenetrating pair of crystals the two origins will be identical, while in the case of a purely juxtaposition twin the two individuals and the centres of their axial systems will be separated at their maximum distance. Between these two extremes all degrees of interpenetration will be met with, and the two crystals and their axial centres must be so placed as to represent faithfully the observed facts.

With these general hints on the drawing of twins the subject of composite crystals may well be left. After having once constructed the two axial systems, the only real difficulty, in accordance with the particular rules among the foregoing which apply to the case under investigation—and most cases will be found to be capable of being tackled by use of one or other of these rules—no further difficulty will be presented; for the process of drawing the two individual crystals themselves will be the same in all cases, and the example, ammonium selenate, given under the first case will suffice as an illustration for all three cases. The contour of the plane of junction of the two individuals is automatically given by the points of meeting of the lines representing analogous and opposite edges on the two drawings. Finally, in investigating a twin, an open mind must above all things be maintained, and the whole structure thoroughly gone into from first principles. For the phenomena of twinning, and of composite crystallisation in general,



are so varied, that something new may be met with at any moment, and the observed facts must be most carefully observed and faithfully recorded. It is hoped, however, that the rules and methods described in the foregoing pages may be of great assistance and guidance in conducting the inquiry concerning this admittedly difficult part of a crystallographic investigation.

## CHAPTER XXIX

### PLANES OF CLEAVAGE AND GLIDING—ASTERISM—CRYSTAL HARDNESS AND ITS VALUATION—CRYSTAL VISCOSITY—THE FOAM-CELL AND PULSATION-CELL THEORIES

AN exceedingly important property possessed by most crystals, and one which is not only developed in a manner characteristic of the particular substance but is also of the greatest value as an indication of internal structure, is that of **cleavage**, the capability of being more or less readily split along definite plane directions, which are usually parallel to certain of the principal faces. If these faces belong to the same form, that is, are of equal value as regards the crystallographic symmetry, the facility of cleavage is equal parallel to all of them, but if there be cleavage developed parallel to the faces of more than one form, then the facility is different for each form. The degrees of facility of cleavage are usually indicated by the terms "perfect" and "imperfect," corresponding respectively to facile splitting and to cleaving with some difficulty. One of the best modes of testing for cleavage is to arrange a pen-knife blade so that its sharpened edge is pressed along the right direction of the firmly held crystal, and then to strike its blunt upper edge smartly with a light hammer. When the "knack" of properly carrying out this operation has once been learnt, the crystal may be cleanly split into two fragments without any crushing or other destructive effect, even if the crystal be one of a fairly soft substance.

A perfect cleavage is quite a special kind of fracture, and is sharply distinguished from the various forms of ordinary fractures, such as the "conchoidal" fracture of glass and ice and of the very imperfectly cleavable quartz, the "hackly" or ragged fracture of native metals, the "uneven" fracture of tourmaline, and the "splintery" fracture of fibrous hæmatite (iron oxide  $\text{Fe}_2\text{O}_3$ ). For a perfect cleavage surface is as truly plane and exquisitely polished as the best natural face, and this fact is of the utmost practical importance, for it affords us the means of determining the position of the cleavage plane or planes, with respect to the crystal faces and the crystal symmetry, on the goniometer itself. An excellent image of the signal-slit is afforded by each of the two cleaved surfaces torn asunder from each other, and when a face of the natural crystal, parallel to which the cleavage has been effected, is present on either or both of the fragments into which the crystal has been cleaved, the image from the cleavage surface will be found

to be situated at  $180^\circ 0'$  from the image reflected from that natural face, in the case of either fragment. Two or three minutes of aberration from this theoretical position are all that are ever observed with good crystals, the limits of error being the same as for goniometrically perfect natural faces.

The two best-known examples of highly perfect cleavage are : (1) mica, of which there are several varieties ; muscovite mica is a silicate of aluminium and potassium,  $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$  ; lepidolite is a similar silicate of aluminium and lithium, and biotite is one of aluminium, iron, and magnesium ; (2) gypsum (selenite), hydrated sulphate of lime  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

The thin cleavage sheets of transparent colourless muscovite mica are now so well known as every-day articles of commerce, being so useful for lamp-shades and similar purposes on account of their non-inflammability and poor conduction of heat, that no further description is necessary. They may readily be obtained thinner than sheets of paper, and the films are flexible ; they thus exhibit cleavage in its most highly developed form, although no trace of it is visible in a well-formed crystal plate, unless the edges have been weathered or injured, as is, unfortunately, however, almost always the case with mica. A particularly

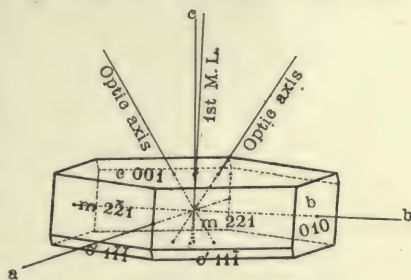


FIG. 430.—Crystal of Muscovite Mica.

good tabular crystal of muscovite mica is shown in Fig. 430, an apparently hexagonal plate. As a matter of fact the simulation of hexagonal symmetry is as extraordinary as in the case of potassium sulphate, and here the real symmetry is not even rhombic, as in that case, but monoclinic. Moreover, the angle  $\beta$  between the vertical axis  $c$  and the inclined axis  $a$  is  $90^\circ 0'$  within the limits of error of measurement, which are not easy to fix in the case of mica on account of the difficulty of finding crystals with perfect edge-faces to the plates ; hence, mica was long thought to be rhombic. The forms shown are the vastly predominating basal pinakoid  $c = \{001\}$ , to which the plates are parallel and which is the direction of cleavage, the clino-pinakoid  $b = \{010\}$ , the negative hemi-pyramid  $m = \{221\}$ , and narrower faces of the positive primary hemi-pyramid  $o' = \{11\bar{1}\}$ . The primary prism  $\{110\}$ , the faces of which are inclined at approximately  $60^\circ$  to each other and to the clino-pinakoid faces, and at  $90^\circ$  to the  $c$  faces, is not usually developed, although  $\{110\}$  is the twin plane of the micas. If present its faces would replace the edges  $mo'$ , and the edges  $pp$  would be truly vertical, parallel to the vertical axis  $c$ .

That the symmetry is really monoclinic was shown by Hintze and Tschermak, who discovered that the ellipsoid, which expresses the values of the refractive index and the optical characters in general in different directions of the crystal, was not situated with its principal axes identical in direction with all three crystallographic axes, as would be the case if the crystal were rhombic, but that it was rotated slightly about the  $b$ -axis, which was common, and so that the axis nearly coincident with the vertical



crystallographic axis was inclined backwards from that axis at an angle of  $1\frac{1}{2}^{\circ}$  to  $2^{\circ}$ .

This fact can readily be confirmed by studying the optic axial interference figure which is afforded when a plate of muscovite mica is examined in the polariscope, between crossed Nicols and in convergent light. The method will be fully gone into in subsequent chapters (XLII. and XLVIII.), and it will suffice to say here that the two optic axes are indicated by the vertices of dark hyperbolic "brushes," arranged like two letters V with rounded apices placed horizontally on each side of the centre of the field thus:  $> <$ , and which are sharply defined curves at the vertices themselves, to which two imaginary vertical lines are tangential, but which spread out as the curve in each case tails away from the centre above and below the horizontal diameter of the field; the vertex marking the optic axis in each case is surrounded by a series of spectrum-coloured interference rings (really curves termed "lemniscates") when observed in ordinary white light, and which become better defined dark rings in homogeneous (monochromatic) light, and which are looped together as figure-of-eight  $\infty$  lemniscates after the first few rings, all passing eventually into enveloping ellipse-like curves (see Fig. 677 on Plate IV. in Chapter XLII.). This beautiful figure is the one seen when the crystal plate is arranged so that the line joining the optic axes is at  $45^{\circ}$  to the crossed rectangular directions of the Nicols. When the plate is rotated  $45^{\circ}$  so as to bring the optic axial line parallel to one of the latter, the hyperbolic brushes rotate about their respective vertices (the optic axes) and become a dark cross, one narrower bar of which joins and passes through the axes while the other broader one crosses this narrower one rectangularly half-way between the two optic axes (see Fig. 676 on Plate IV.). The lemniscates, however, retain their general appearance. It will be obvious that the plate necessary to afford this interference figure symmetrically placed to the centre of the field must be one either naturally developed, or artificially cut out of the crystal, perpendicular to the bisectrix of the angle (the acute one) between the optic axes. Now this bisectrix is one of the principal axes of the optical ellipsoid, and in a rhombic crystal it would be identical with one of the three crystallographic axes, for these three latter are identical in direction with all three axes of the ellipsoid.

In the interesting case of muscovite mica, it is a fortunate fact for the ease of observation of the optic axial interference figure, that the acute bisectrix is almost perpendicular to the direction of cleavage, so that a cleavage plate of the right thickness (that of a piece of card) shows the figure apparently symmetrical to the centre of the field, and recourse to the cutting of a plate is unnecessary. Obviously also a natural tabular crystal of the same thickness shows it equally well. For many years it was thought to be absolutely symmetrical to the centre, but the work of Hintze and Tschermak made it certain that the bisectrix is inclined at an angle not exceeding  $2^{\circ}$  backwards from the normal to the cleavage plate. Hence, the crystal must be monoclinic and not rhombic, and is therefore to be described as monoclinic with a strongly pseudo-hexagonal habit.

In order to render the symmetry of muscovite mica and the relations

of the optic axes to it clear, the directions of the crystallographic axes  $a$ ,  $b$ , and  $c$  are indicated in Fig. 430, as are also those of the two optic axes and their bisectrix, which latter is also called the first median line (and is therefore marked 1st M.L. in the figure), to distinguish it from the bisectrix of the obtuse angle (the supplement of the acute), which is called the second median line, and is identical in direction with the crystal-axis  $b$ . The amount of deviation (from identity with the vertical axis  $c$ ) of the first median line is exaggerated in order to render it clear. In reality, on the scale of the figure, it would appear identical with axis  $c$ . This line marked 1st M.L. is the only line in the figure not drawn exactly to scale; the crystal itself is drawn to the exact axial-ratio dimensions. It will be noted that the optic axes are separated in a plane at right angles to the plane of monoclinic symmetry, the latter being  $b = (010)$  containing the axes  $a$  and  $c$ , which in this remarkable case are inclined at an angle  $\beta$  which is  $90^\circ 0'$  within the error of possible determination, although it is probable that if that error could be reduced, by the discovery of crystals with perfect edge-faces, it would be found to differ by a few minutes from  $90^\circ$ .

It is interesting also that the symmetry plane  $b = (010)$  is indicated by one of the three lines inclined at  $120^\circ$ , making up a star of six rays inclined at  $60^\circ$ , which form the well-known "**percussion figure**" of mica, which is produced by indenting a plate of mica with a sharply pointed punch, struck smartly by a light hammer; moreover, the particular ray of the star parallel to the symmetry plane is usually much more strongly developed than the others parallel to the  $m$ -faces  $\{221\}$ . So that both the percussion figure and the optic-axial interference figure at once enable the direction of the symmetry plane to be ascertained in a cleavage plate of mica, when no natural edges are present on the margin of the plate. The percussion figure is quite distinct from the "pressure figure" described on page 531 and from the phenomenon of "asterism" which is exhibited by the variety of mica known as phlogopite, and which will be found dealt with on page 533.

The separation of the optic axes in muscovite mica varies from  $60^\circ$  to  $75^\circ$  as seen in air, but the true angle within the crystal is smaller, the difference between the true and apparent angle being due to the different refractive indices of the crystal and air. The exact angle differs also for different wave-lengths of light, being greatest for red light and least for violet light. An angle in air of  $60^\circ$ - $75^\circ$  is one that is very convenient in size for the demonstration of the rings and brushes round the optic axes of biaxial crystals, as the whole figure can be seen at once in most ordinary wide-angle polariscopes. Hence mica is a very favourite substance for the demonstration of this very beautiful optical phenomenon, and all this is due to the development of such perfect cleavage in a direction which is so fortunate for the display of the phenomenon.

In some of the other varieties of mica, biotite for instance, the separation of the optic axes is so small that they were formerly thought to be uniaxial; indeed biotite was named after Biot, who described it so long ago as 1816 as uniaxial. In all cases, however, the apparently



single axis, really the bisectrix of a very small angle, is never quite perpendicular to the cleavage plate, that is, to the basal pinakoid; the axes, moreover, are separated at this minute angle in the symmetry plane and not perpendicular to it as in the case of muscovite, and the angle for red light is the least instead of the greatest. Extreme cases have been described in which the deviation from the normal to the cleavage plane has been as much as  $8^\circ$  in the cases of these so-called uniaxial micas. Lastly concerning mica, the first median line moves in the symmetry plane on raising the temperature, another proof that the symmetry is monoclinic and not rhombic; for if it were the latter, the bisectrix would be identical with the crystallographic axis  $c$  for all temperatures, as symmetry is independent of temperature, change of temperature leaving the symmetry unimpaired.

Gypsum (selenite),  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , a typical crystal of which is shown in Fig. 400 in the last chapter, is also an instance of a monoclinic mineral having a perfect cleavage, which in this case is parallel to the symmetry plane  $b = (010)$ . Films of great tenuity can be obtained as in the case of mica, and such selenite films are largely used for optical purposes, being very convenient for the production of interference colour-tints in plane-polarised parallel light, and for determining the sign of the double refraction of such crystals as are bi-refrangent. These uses will be fully explained in a subsequent chapter (XLII., see Fig. 662), together with the reason for the succession of colour-tints which selenite films display in polarised light according to their thickness, and for the distinction between tints of the first, second, third, and higher orders. The symmetry plane, besides being the plane of cleavage, also contains the two optic axes, separated at an apparent angle in air of about  $100^\circ$ . Hence the optic axial interference rings and brushes are not seen on looking through a cleavage plate of selenite placed in the convergent light polariscope, a section-plate requiring to be cut at right angles to the symmetry plane and perpendicular to the acute bisectrix of the optic axial angle in order to produce them; this is an operation of some difficulty, as it is across the direction of the very facile cleavage, instead of being parallel to it as in the case of mica. Selenite will be taken as a special example of optic-axial-angle phenomena later on, as it is one of the most remarkable substances known to us from this point of view, showing among other things extraordinary sensitiveness to change of temperature.

Many other minerals cleave so readily that they are frequently found in the form of their cleavage solid. This in the cases of mica and selenite would simply be a plate, as the cleavage is parallel to a form of the monoclinic system which in each case consists of merely a pair of parallel faces, the clino-pinakoid  $b = \{010\}$  in the case of selenite, and the basal pinakoid  $c = \{001\}$  in the case of mica. But in the case of calcite, for instance, the cleavage occurs parallel to the faces of the primary rhombohedron  $r = \{100\}$  (which is, in fact, taken as such because it is so obviously important with regard to the internal structure), and the mineral is very commonly found in such cleavage rhombohedra; whereas a complete natural crystal, which could be distinguished by the presence



of small faces of other forms modifying its edges, such, for instance, as the crystal shown in Fig. 296, in Chapter XXII. page 343, is rarely found of the primary rhombohedral habit, the other rhombohedron of calcite  $e = \{110\}$ , Fig. 294, being on the other hand very common, as is also the scalenohedron  $v = \{201\}$ , Fig. 287, well seen in the form of calcite known as "dog-tooth" spar shown in Fig. 4 on page 7. The cleavage rhomb of calcite is an excellent illustration of the fact that cleavage occurs equally well along all the planes belonging to a form, in this case three.

Cleavage directions are obviously those of minimum cohesion, and the laws governing the symmetry of crystals are applicable as much to the force of cohesion exerted in different directions within the crystal structure, between the particles composing that structure, as to the exterior facial planes; for both are equally dependent on the structural arrangement of the particles, that is, on the nature of the space-lattice formed by their representative points or centres of gravity.

Another instance is the octahedral cleavage of the diamond, the cleavage occurring absolutely equally along the four planes of the regular octahedron  $o = \{111\}$ , the eight faces of which obviously comprise only four different planes, for opposite pairs of faces are parallel; and each cleavage surface would be found to be situated at precisely  $180^\circ 0'$  to the face of the octahedron to which it is supposed to be parallel, if that face were developed in good measurable condition (and not curved, as is so often the case with the diamond) on the same fragment.

The little cubes into which galena, sulphide of lead  $PbS$ , so readily cleaves, and which may be reduced down to microscopic dimensions, afford another excellent instance of three planes of cleavage being equally developed parallel to the whole of the faces (here six, falling into three pairs of parallel faces) of a form, the cube  $a = \{100\}$ .

From the foregoing it will have become clear that cleavage is not a mere tendency to fracture with production of two more or less plane fracture-surfaces, one on each of the two separated fragments, and along an approximately definite direction. Cleavage is much more than this, namely, the facility for splitting along an absolutely true plane, having an orientation within the crystal definitely fixed to one or two minutes of arc, and which definite direction is identical with that of an important face of low indices, very often a primary one, to within the same minute limit of accuracy as natural faces exhibit when grown undisturbed; and the plane surfaces of fracture are endowed with the same high degree of natural polish as the best formed faces, and afford equally sharp and brilliant images of the signal-slit of the goniometer. If more than one face or pair of parallel faces constitute a form, as in the systems of symmetry higher than the triclinic, as many such cleavage directions are developed as there are planes—each of which may correspond to two parallel natural faces, one on each side of the crystal—constituting the form in accordance with the degree of symmetry exhibited by the crystal. Moreover, compared with the facility for splitting along the cleavage plane or planes, the crystal usually offers relatively enormous resistance to fracture along any other direction, and when it does occur the fracture

is very irregular, and indeed is very frequently stepped or zigzagged, the steps or zigzags being composed of an alternation of irregular unreflective bits of crystal surface and of little true planes having the direction of the nearest cleavage plane characteristic of the crystalline substance, and which is, of course, oblique to the direction in which it was attempted to cleave the crystal. The fracture may also be rough or "hackly," as in the cases of many metals, or shell-like or "conchoidal" as in the case of quartz. But a crystal of a substance endowed with a good cleavage may be smashed up to small fragments or even to a coarse powder, and yet these fragments will mostly display cleavage surfaces yielding good signal-images.

The cleavage cube of galena, the cleavage octahedron of the diamond, and the cleavage rhomb of calcite, are all obviously closed forms, so that a cleavage solid results entirely from one "cleavage," using the term in its fullest significance. But in the systems of lower symmetry, it may require three different "cleavages" (forms) to produce a closed solid, each corresponding to a form of two parallel faces and therefore of one plane. All three, however, may not be developed, and even if they are, their degrees of facility will be different. In many cases not more than two of them are developed, thus giving rise to an open prism by cleavage, terminated by natural faces. The same result is produced when the symmetry is such that a single form, parallel to which there is cleavage, consists of four faces, two pairs of parallel faces, so that here one cleavage would produce the prism. In a large number of cases, however, only one cleavage is developed, and parallel to a form comprising only a pair of parallel faces, giving rise to a plate by full exercise of the cleavage, having natural faces for its edges. Such a case is that of mica, as also that of gypsum.

A concrete case of the intermediate order is afforded by our typical rhombic crystal of potassium sulphate, which possesses two directions of cleavage, a fairly perfect one in the direction of the brachy-pinakoid  $b = \{010\}$  and a less perfect one parallel to the basal pinakoid  $c = \{001\}$ , both being single-plane forms composed of two parallel faces in accordance with rhombic symmetry.

The cleavage form is not necessarily that of the crystal. Thus fluor-spar, calcium fluoride  $\text{CaF}_2$ , is frequently found in simple cubes, but its perfect cleavage is octahedral, and the corners of the cube may be readily split off until the crystal resembles a combination of the cube and octahedron in equipoise; and the process can, of course, go further until nothing but a simple cleavage octahedron remains.

**Connection between Cleavage and Structure.**—In the next chapter (XXX.) it will be shown that a crystal is a homogeneous structure composed of an assemblage of ultimate structural units, the chemical atoms, which may be considered as represented geometrically by analogous points within them, their centres of gravity for instance, each of which may be considered as standing for the sphere of influence dominated by the atom. These ultimate structural-unit-points will further be shown in the general case to be arranged on the plan of one of the 230 point-systems, which the geometricians have unanimously agreed represent the



arrangement of the only possible types of homogeneous structure; and also to be grouped about the nodes of an underlying or fundamental space-lattice, or (otherwise expressed) to make up an interpenetrant, or otherwise disposed, number of precisely similar space-lattices, the number corresponding to that of the atoms composing the molecule or small group of molecules—the grosser structural unit—of the crystallised substance. It will be proved, moreover, that it is the form of the space-lattice which determines the system of crystalline symmetry, the elements and interfacial angles, and the concordance with the law of rational indices, while the particular class of symmetry within the system is determined by the nature of the groups about the nodes, or of the interpenetrating, or otherwise arranged, combined assemblage, that is, by the arrangement of the atoms forming the grosser structural unit (the crystal-unit), the chemical molecule or polymolecular group. To make this somewhat intricate but very essential point quite clear, any particular atom (or its representative point) of the molecule or polymolecular group may be considered as the point representing the whole grosser structural unit, so long as in every molecule or polymolecular group, whichever forms the grosser structural unit, of the assemblage the analogous atom is also chosen, and these analogous atoms form the space-lattice, so that there are as many similar space-lattices as there are atoms in the chemical molecule or polymolecular crystal-unit; the intramolecular arrangement of all the adjacent atoms in the assemblage which together correspond to the chemical formula of the substance, or in the group of molecules if the crystal-unit be polymolecular, and which molecular or polymolecular arrangement is repeated throughout the whole assembly as often as there are points in the space-lattice, determines the details of the symmetry, that is, the particular class.

Thus we arrive at the important conclusion that the molecules or molecular groups—considered as the grosser or crystal-structural units and as each, therefore, corresponding to one point of the fundamental point system—are built up to form the crystal edifice on the plan of a space-lattice, and the architecture of this decides the crystallographic system; while the stereographic arrangement of the atoms in the molecule or group, that is, the architectural plan of the internal structure of the molecule or polymolecular crystal-unit itself, fixes the particular class of the 32 possible classes to which the crystal shall conform. It must thus be clearly understood that it is neither the atom nor the molecule which determines the class, for as we have seen, if we take any atom (each atom in turn if desired) of the molecule or crystal-unit group, this, together with analogous atoms taken from all the molecules or groups, only gives us again the space-lattice and crystal system; and the same result is again attained by considering not a particular atom but any point such as the centre of gravity as representative of the whole molecule corresponding to the chemical formula, or of the small group of molecules in the event of the crystal-unit being polymolecular. It is on the contrary the **stereographic** arrangement, the geometry of the distribution in space, the mode of grouping about the nodes of the space-lattice, of the



whole of the atoms composing the crystal-unit, or what comes to the same thing, the stereographic mode of interpenetration or other disposition of the atomic space-lattices, which determines the class.

Now in a space-lattice all parallel planes are of identical structure, and are separated from each other at equal intervals. But the different sets of parallel planes, at different inclinations to each other, in the space-lattice, differ in the number of points, representing the molecules, or polymolecular groups, or a particular atom in each of the molecules or groups, which they contain in a given area; that is, some planes are more thickly strewn with points than others. Moreover, those in which the points are most thickly congregated are furthest separated from the parallel planes nearest to them. Now all the evidence up to the present accumulated goes to show that the commonest faces characteristic of a crystallised substance are those parallel to planes most densely strewn with points, that is, with structural units, be they considered as whole molecules or groups or specific atoms; also that the cleavage planes correspond to those planes of the space-lattice which are the most widely separated from each other. For obviously the cohesion should be a minimum between particles at the greatest distance apart, and a maximum between those nearest together, in accordance with the universal law of inverse squares applying to forces of this description between particles. Hence, the fact that the directions of cleavage are usually those of the commonly developed crystal forms is in perfect agreement with the theory of crystal structure which will be established in Chapter XXX. It also now becomes perfectly clear why cleavage can only occur along certain specific plane directions identical with forms of low indices, for it can only occur along a plane or planes of the space-lattice. Further reference to this subject will be made in Chapter XXXI., when considering the 14 space-lattices, the types of cleavage characteristic of each of which will be described.

**Practical Mode of investigating Cleavage.**—The mode of testing a new substance for cleavage has been already incidentally referred to. It consists in attempting to split a crystal of not too small a size and which is rigidly supported or held during the operation—say by placing it with a broad face, supposing one to be developed, perpendicular to the direction to be tested for cleavage, on a small block of hard wood resting in turn on the steady working bench or table—by means of a penknife blade used as a miniature wedge. The blade is laid with its face upright, and its edge horizontal and firmly pressed downwards on the crystal without cutting, and along the direction it is desired to test. The upper blunt edge of the blade is then struck a smart blow with a very light hammer, when, if the direction be really one of perfect cleavage, the crystal will fall away on each side into two halves, with the minimum of actual cutting by the knife along the edge of application, the minute fissure made affording the blade-wedge the opportunity for pressing asunder the two parts of the crystal along the cleavage plane; the vastly preponderating portions of the two cleaved surfaces do not touch the knife at all, and are thus quite uninjured by the operation when skilfully performed. The two

fragments should then be placed in succession on the goniometer, and the signal-images reflected from the cleavage surfaces examined. If sharp and clear single images are observed to be afforded, there can be little doubt that a real cleavage direction has been discovered; and if several repetitions of the operation on different crystals yield the same result, any lingering trace of doubt disappears. The position of the signal-image should in each case be determined with respect to that of the face parallel to which it was endeavoured to produce a cleavage, and when the cleavage direction is what it was supposed to be, it will be found that the angular difference between the readings for the cleavage surface and this natural face on the same fragment will be within a couple of minutes or so of  $180^{\circ} 0'$ , the deviation depending probably more on the character of the natural face than on that of the cleaved one. No true investigator will be satisfied, of course, with a single experiment and measurement; all the crystals of a substance should show the property in common, and therefore specimens from several different crops should be tested, say four or five. If all unite in giving a like result, the cleavage direction may be regarded as well established. The facility of the cleavage should, needless to say, be noted, in order that it may be described, for the benefit of future observers as well as for reasons connected with a true appreciation of the structure, as "perfect" or "imperfect." The character of the signal-images will assist materially in deciding whether it is to be described as the one or the other, an imperfect cleavage rarely yielding such sharp single images as a perfect one. Moreover, when the direction corresponds to a face of a crystallographic form comprising more than one pair of parallel faces, the cleavage in both or all three planes of the form ought to be tested on one of the larger crystals available, in order to confirm the fact that cleavage occurs along all the planes of the form.

**Glide-Planes.**—Crystals which are not high in the scale of hardness often show another property dependent on the internal structure, somewhat akin to cleavage, which involves a permanent deformation of the crystal, namely, that of possessing planes of gliding of the structural particles over one another, under the influence of a moderate amount of force. These planes are most frequently, but not always, identical with the planes of cleavage. They were discovered in the investigation of "pressure" figures by Reusch, who invoked them by pressing the blunt point of a conical steel punch on the crystal surface and striking it with a light hammer, just as for the production of the percussion figure of mica. The punch or cone, however, requires to be bluntly and not sharply pointed in order to produce these pressure figures, and the crystal is best laid on an elastic surface and not on a rigid one. In the case of mica, which shows the phenomenon well, this "**pressure figure**" consists of a six-rayed star similar to the percussion figure described on page 525, but the rays are perpendicular and not parallel to the edges of the plate and bisect the angles between the rays of the percussion star. They indicate **planes of gliding** parallel to the faces of monoclinic pyramid forms.

Rock salt, sodium chloride  $\text{NaCl}$ , which crystallises in cubes and

belongs to class 32 of highest crystal symmetry,<sup>1</sup> affords a still better example of a crystallised substance possessing planes of gliding. Again they are not parallel to the cleavage planes, which are those of the cube,  $\{100\}$ , but are on the contrary parallel to the six planes of the rhombic dodecahedron  $\{110\}$ .

By far the most interesting case, however, is that of calcite, in which the phenomenon was discovered by Reusch, and a most remarkable method of developing the sliding movement in which was subsequently described by Baumhauer, which is illustrated in Figs. 431 and 432. A cleavage rhomb of calcite is taken, such as that represented in Fig. 431, and laid so that the position of the trigonal axis, usually vertical, is as indicated in the figure, one set of polar edges, the longer ones of this particular rhomb, being brought horizontal and so that the plane  $edh$  is also horizontal. The crystal should be held firmly in this position in a vice with soft wooden or cork-lined jaws. A knife blade is then pressed downwards and slightly sideways towards  $c$ , and with

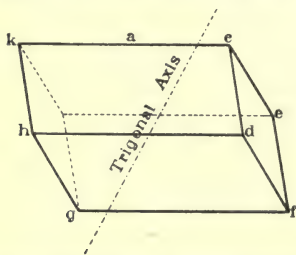


FIG. 431.—Cleavage Rhomb of Calcite arranged for Glide-Plane Experiment.

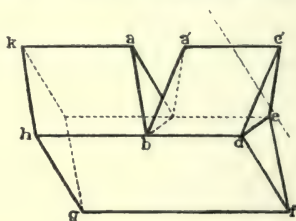


FIG. 432.—Result of Glide-Plane Experiment with Calcite Rhomb.

the edge horizontal, at about the middle point  $a$  of the upper edge of the rhomb. It is then observed that layer after layer of crystal substance parallel to the plane  $edh$  moves away in the direction of the sideward pressure, and if the force on the knife be adequate to cause it to reach the centre of the crystal, an apparently perfect reflection twin is produced; for the moved portion  $a'bc'de$  (Fig. 432) is the exact counterpart of the portion of the original crystal which lies below it, as if the latter were reflected at the plane  $edh$ . This latter plane is parallel to one of the faces of the other common rhombohedron of calcite  $e = \{110\}$ , which replaces the polar edges of the primary one  $r = \{100\}$ , to which the cleavage planes are parallel, shown in Fig. 431. The glide-planes of calcite are, therefore, parallel to the faces of  $e = \{110\}$ , and the term secondary twinning has been given to this kind of twin formation, to distinguish it from ordinary natural twin growth. The glide-planes are thus again distinct from the cleavage planes. In the cases of many other crystals, however, they are identical with the cleavage planes.

It is very interesting to inquire what has happened during this apparently simple push-movement of the particles along glide-planes. If we investigate the physical properties of the newly placed part  $a'bc'de$

<sup>1</sup> See page 154 regarding recent work on the symmetry class of rock salt.



of the calcite crystal (Fig. 432), we shall find that the position of the single optic axis (the crystal being trigonal and therefore optically uniaxial) has changed with the movement. It was formerly situated as shown in the broken-and-dotted line in Fig. 431, the optic axis being identical with the trigonal axis, but it is now rotated over in the same vertical plane *efgk* to the position shown by the broken-and-dotted line in Fig. 432. In other words, the corner *c'* is now no longer a polar solid angle but an equatorial one, of the same character as that at *f*. The actual amount of rotation of the optic axis from one position to the other is  $52\frac{1}{2}^\circ$ , while the angular movement of the face *cde* is  $38^\circ$ . In order to account for this there must not only be a transference but a rotation of the particles, probably corresponding in amount to the angular change of the optic axis. Voigt has further shown from determinations of the elasticity of calcite in different directions, that the glide-plane corresponds to one of the two mutually perpendicular planes of minimum resistance to elastic movement of the crystal particles; but this is not sufficient to account altogether for the glide-plane, for the second plane of minimum resistance at right angles to the first is not a glide-plane. Hence there can be no doubt that there is another factor concerned in the operation, and that rotation of the particles occurs as well as the elastic movement of transference. It is highly interesting in this connection that Reusch observed that in order to get the gliding of a particular lamella to occur it was necessary to overstep a certain limit of force, and that if the force stopped short of this the lamella moved back again by its purely elastic force, no permanent deformation being suffered. Hence the weaker force can only have brought about the elastic movement along this plane of minimum resistance, but when the critical force was exceeded rotation of the particles occurred, and no return was then possible, the deformation being a permanent one.

The phenomenon of **Asterism** presented by some calcite crystals is connected with the secondary twinning or gliding parallel to the faces of  $e = \{110\}$ . When a candle flame is viewed through such crystals or cleavage fragments it appears as a radiating star of light. The effect is due to large numbers of minute hollow tubes, parallel to each other in three directions; they would appear to have been produced where the gliding *e*-surfaces intersect one another.

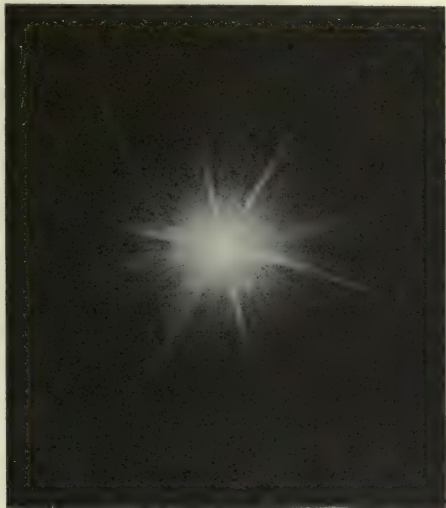


FIG. 433.—Asterism of Phlogopite.

Asterism is very commonly shown by the magnesia mica known as phlogopite, a yellow or brown variety of mica sometimes found in rough prisms or pyramids. A reproduction of an admirable photograph taken by Professor H. Stanley Allen of a spot of light viewed through a cleavage flake of phlogopite is given in Fig. 433. There are six very distinct rays to the star, and an indication of six other intermediate rays (two of them very clearly defined). The effect is due to fine inclusions along the glide planes parallel to the faces of a monoclinic pyramid form.

Asterism is also well known in connection with certain sapphires, the blue crystals of corundum,  $\text{Al}_2\text{O}_3$ . These "asteriated" or "star" sapphires were mentioned by Pliny. They exhibit a six-rayed opalescent star when viewed nearly but not quite in the direction of the principal (trigonal) axis; jewellers cut the stones *en cabochon* (with a curved surface), which facilitates the display of this much prized effect. In this case also the asterism is due to minute cavities of tubular character arranged in planes parallel to the hexagonal prism of the second order  $\{10\bar{1}\}$ . They are probably caused by corrosion (solution), which occurs somewhat readily in corundum along these second order prismatic planes, often giving rise to a pseudo-cleavage or "parting" (not a true cleavage) parallel to these planes.

#### HARDNESS OF CRYSTALS AND ITS VALUATION.

The **Hardness of a Crystal** is measured by its capability of being just abraded or scratched by contact with a sharp fragment of another substance of slightly greater hardness, and of which the degree of hardness is known with reference to a conventional scale. Hardness, as thus measured, is a highly characteristic crystallographic property. It has been defined by Dana as "the resistance offered by a smooth surface to abrasion." What occurs during the abrasion is that the particles of the softer substance are torn away by the harder substance, in the form of powder, their cohesion being overcome. Hence, hardness is intimately connected with cohesion, and therefore with the structure of crystals.

Most artificially prepared crystals, such as those of metallic salts or other chemical preparations, are low in the scale of hardness, and the determination of their hardness is not of much value. But in the case of naturally occurring mineral crystals, usually higher in the scale, the degree of hardness displayed is frequently a most valuable help towards identification. Thus the diamond is uniquely distinguished by remaining unabraded by any other substance, a sharp fragment of another diamond being alone capable of scratching it. The hardness of the diamond is thus obviously the maximum known. The diamond is, therefore, placed at the head of the scale of hardness. This scale has ten units, corresponding to the ten distinctly marked degrees of hardness of certain specific minerals. The substances are stated in the following table in ascending order of their hardness. It is usually known as Mohs' scale of hardness, the order having first been definitely arranged by F. Mohs.

## MOHS' SCALE OF HARDNESS.

- |               |                        |
|---------------|------------------------|
| 1. Talc.      | 6. Orthoclase felspar. |
| 2. Gypsum.    | 7. Quartz.             |
| 3. Calcite.   | 8. Topaz.              |
| 4. Fluorspar. | 9. Corundum.           |
| 5. Apatite.   | 10. Diamond.           |

The degree of hardness is experimentally determined by observing that the crystal under investigation is just able to be scratched by a particular one of these minerals forming the scale of hardness, and which is therefore above it in the scale, and itself scratches the mineral next below in the scale. For instance, a crystal which is scratched with some little difficulty by quartz, but which is itself capable of scratching orthoclase felspar, is possessed of a hardness between 6 and 7. Talc and gypsum are so soft as to be scratched by the finger nail. A penknife is a most useful article for testing hardness; for good steel has a hardness of about 6, and so will not scratch quartz, but readily scratches any mineral below orthoclase in the scale. The three varieties of corundum, aluminium oxide  $\text{Al}_2\text{O}_3$ —the ruby, sapphire, and emery—are only slightly less hard than the diamond, and are absolutely impervious to the penknife, the point of which they will readily blunt; but glass imitations of these gem-stones have a hardness about 6, and are just scratched by the knife. In the absence of a diamond, glass can often be scratched by a sharp fragment or pyramidal point of a quartz crystal, sufficiently to break readily along the line of scratch.

It must not be overlooked, however, that the hardness varies slightly with the cleavage direction, being always lower along the direction of cleavage than in the direction perpendicular thereto. High specific gravity, that is, great density, is generally accompanied by great hardness, as it is also as a rule by a high refractive index.

The following definition of Hardness was contributed by the author to the Report of the Hardness Tests Research Committee of the Institution of Mechanical Engineers, published in 1916, of which Committee the author was a member:

“The hardness of a solid substance may be defined as the resistance offered by a smooth surface of the substance to abrasion. It is measured by the capability of the substance being just abraded or scratched by contact with a sharp fragment of another substance of slightly greater hardness, and of which the precise degree of hardness is known with reference to a conventional scale. Particles of the softer substance are torn away by the harder, their cohesion being overcome. Hence, hardness is intimately connected with cohesion. If the solid substance be crystallised, the hardness varies slightly with the direction within the crystal, as cohesion in a crystal is in general dissimilar in different directions; thus hardness is always lower along a direction of cleavage than along the direction perpendicular thereto. For cleavage planes are planes of points of the crystal space-lattice which are most densely strewn with points, and in which cohesion is, therefore, a maximum, while successive



parallel planes of points (all parallel to the plane of cleavage) are the most widely separated from each other, the points being farthest apart in the direction at right angles to these planes; the cohesion is, therefore, a minimum perpendicular to the plane of cleavage. The particles are, consequently, more readily torn off from a cleavage face than from any other face of a crystal. Moreover, high specific gravity (density) is generally accompanied by great hardness. For (considering the case of the perfect solid—a crystal), the points of the space-lattice being the closer together the denser the substance, greater difficulty is naturally experienced in overcoming their cohesion, in accordance with the usual laws governing the attractive forces between particles.”

It should be clearly understood that in this definition of Hardness only truly homogeneous solids are dealt with, the ideal case met with in a single crystal individual perfectly formed, but rarely, if ever, attained or even desired in industrial preparations of metals and alloys. It must be particularly borne in mind that only the perfect solid—a crystal—is referred to in the statement that high specific gravity, density, is generally accompanied by great hardness. Comparisons, for instance, of steels or of rocks are absolutely excluded, for they are non-homogeneous, besides being composed of innumerable individual crystals which, even when of similar or identical chemical constitution, are promiscuously orientated with respect to each other.

The case of diamond, with the maximum hardness 10 but specific gravity only 3·5, and of barytes with hardness only 3, yet a specific gravity of 4·5, is obviously a notable exception to any sweeping generalisation as to hardness accompanying density, and the statement concerning it in the above definition only contemplates cases in which other things are more or less equal, cases of more or less similar constitution. For instance, the two crystalline forms of carbon itself, diamond and graphite, of densities 3·52 and 2·29, and hardnesses 10 and 2; aragonite and calcite, the two crystalline forms of  $\text{CaCO}_3$ , of densities 2·95 and 2·72, and hardness 3·8 and 3·0; and the three forms of  $\text{TiO}_2$ —rutile, brookite, and anatase—which are endowed with the densities 4·26, 4·15, and 3·90, and the hardnesses 6·3, 6·0, and 5·8. Corundum  $\text{Al}_2\text{O}_3$  (sapphire and ruby) is also an excellent example of a crystalline substance involving no heavy metal, yet possessing both high density, 4, and great hardness, 9.

Hardness appears to be closely related to atomic or molecular volume. The connection was pointed out in 1852 by Kennigott, and amplified in 1868 by Schrauf, who showed that cubic substances of analogous composition and series of isomorphous chemically similar substances exhibit degrees of hardness inversely proportional to their molecular volumes. Thus in the cases of galena  $\text{PbS}$ , Greenockite  $\text{CdS}$ , and zincblende  $\text{ZnS}$ , the molecular volumes are 31·8, 29·9, and 24·0, and the hardnesses are 2·5, 3·3, and 3·8. These facts were considerably supplemented and the general principle confirmed by Turner in 1909.

The powder scratched off a coloured or opaque crystal by a harder substance frequently possesses a characteristic colour, known as the “Streak.” The streak is best recognised by spreading and smearing the

powder on white paper. The colour of the streak is often more distinctive of the particular mineral than the colour of the mineral itself.

**Exact Measurement of Hardness by the Sclerometer.**—The most precise measurements of the hardness of crystals yet possible are obtained by the method of Pfaff with the instrument known as the “Sclerometer.” The instrument is seen in Fig. 434 as constructed by Steeg and Reuter.

It consists of a horizontal goniometer-circle divided directly into single degrees, with the crystal-adjusting apparatus carried immediately above it and terminating in a little tabular support on which the crystal can be cemented. The non-rotatable basal table and central axial cone for the independently rotatable circle and crystal-holder is mounted on three wheels rolling on three corresponding guiding rails. The traverse is brought about by laying a convenient weight in a pan connected by a

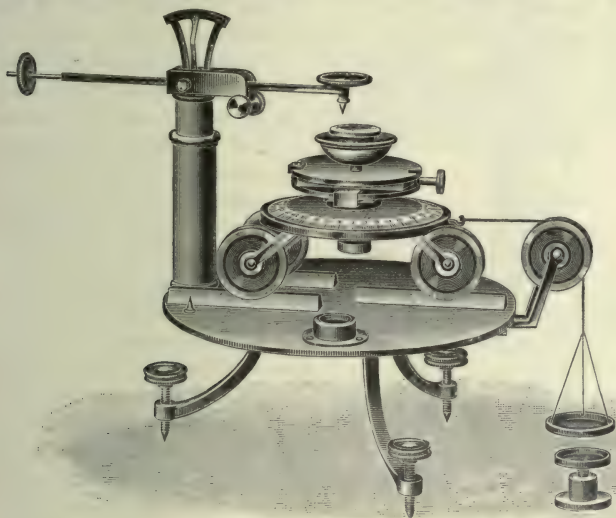


FIG. 434.—The Sclerometer (Steeg and Reuter).

cord with the goniometer table, and passing over a pulley. The fixed tripod table which carries the rails is also fitted with a spirit level, and a vertical column rises from it near the edge, which carries the balance beam, to the end of one arm of which the scratching point is attached. Two alternative points are given, one of which is shown in position and the other lying on the tripod table; one is of hardened steel and the other is of diamond. It is carried at that end of the balance beam which comes over the centre, a little pan for the reception of weights being arranged immediately above it, in order that the scratching may occur with a given pressure. The other arm of the balance carries an adjustable counterpoise for the weight of the pan and scratching point. An adjustable stop is arranged to prevent the point from cutting too deeply into the crystal. In order to provide for crystals of different sizes the supporting column of the balance is adjustable for height, by sliding in an outer pedestal column.

A similar instrument is also supplied by Fuess, the centring and adjusting movements for the crystal being the same as those on the No. 2a goniometer, but which is otherwise constructed on lines

resembling those of the Steeg and Reuter instrument. It is shown in Fig. 435.

The crystal is fixed upon the adjusting apparatus with the face to be tested uppermost, and the load on the little pan above the diamond

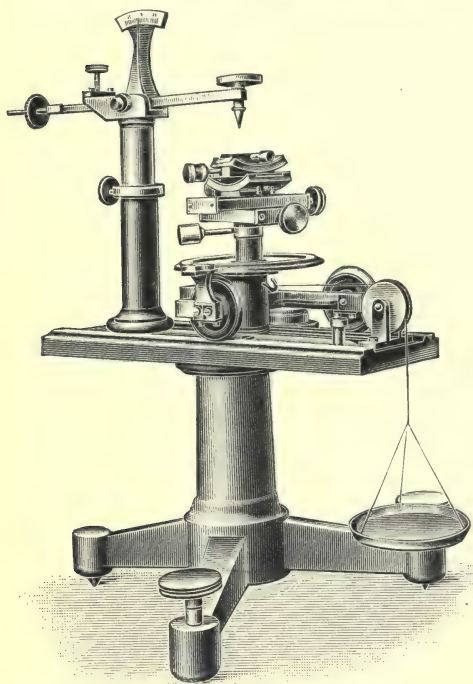


FIG. 435.—The Fuess Sclerometer.

increased until the point of the diamond resting on the crystal surface just scratches it as the crystal is drawn underneath it by the traversing of the goniometer, under the influence of a weight in the pan suspended from the cord. After raising the diamond again the goniometer circle is rotated for some definite angle, and another scratch made, the process being repeated until the scratching effect for all kinds of azimuths of the crystal surface has been tested, the minimum load required to produce a scratch in each direction having been recorded. A drawing of the crystal face is then made, and lines drawn from the centre of it along each experimental direction, of a length proportional to the observed hardness, their terminations being arranged so as not quite to reach the

boundary lines representing the crystal face; these terminations of the lines are then joined by a curve, the **Curve of Hardness**. Such a curve will exhibit the symmetry of the system. For instance, the curve of hardness on the face (111) of calcite perpendicular to the optic axis is a three-leaved rosette, with maxima  $120^\circ$  apart, and minima at the half-way positions; that for a cube face is a square with rounded corners or maxima, and with depressions or minima in the middle of each side.

A somewhat more delicate and accurate modification of this method has also been introduced by Pfaff, according to which the load on the diamond point is kept constant at a weight adequate to effect a convenient depth of scratch, and the traverse is performed for a definite number of times, a hundred or more, the diamond being only allowed to come into operation during the movement in one and the same direction; the amount of material scratched off is then determined by the loss of weight of the crystal, which with its attached crystal-holder is carefully weighed before and after the experiment. The hardness is



then considered to be inversely proportional to the weight of crystal dust thus removed.

A delicate form of sclerometer for use with the crystallographic microscope, such as the Dick microscope or the No. 1 Fuess instrument, has been described by Jaggard,<sup>1</sup> which he terms a "microsclerometer." It is supplied with a rigid standard and with apparatus for adjusting the instrument to the microscope; also with rotating, lifting, and fixing adjustments, a balance beam with a rotatory diamond at one end, and a recording apparatus for the number of revolutions of the diamond and the depth of its penetration. It is capable of measuring variations of the rate, depth, or duration of the scratching, as well as of recording very accurately the weight above the diamond point. The operations are watched under a low-power objective of the microscope. Almost all the varieties of modes of procedure which have from time to time been described may be followed with this instrument, involving abrasion, penetration, friction, and fracture. Further details, together with an illustration (Fig. 841a) will be given in Chapter LII. on the crystallographic microscope.

The determination of the hardness of a crystal—which, if perfectly formed, is essentially a homogeneous body the properties of which are always the same in any specific direction with respect to the crystal morphology, and in all directions which have the same significance with respect to the symmetry—is quite a different problem from that of the hardness of a metal or alloy employed by the engineer. Unfortunately, the two problems have been too frequently confused together. For an engineering or armament material is often quite specially surface-hardened or designedly given a superior hardness in the parts to be exposed to forces of impact or wearing, and is consequently essentially unhomogeneous. Moreover, it usually consists of a compact mass of crystals interlacing and interlocked with each other in every possible different orientation, so that the hardness result can at the best be only an average one, and not correspond to any definite crystallographic direction. Methods of testing such hardness have been devised for these industrial purposes which, although quite unsuitable for the determination of crystal hardness, are not without interest to the crystallographer, and throw considerable light on the general problem of hardness. Such are (a) the indentation tests, in which the surface of the material under test is permanently distorted by the pressure of a hard steel ball, cone, or knife-edge, namely, the Brinell ball test, the Ludwik right-angled cone test, and the Shore scleroscope hammer test; and (b) in a less degree the resistance-to-wear tests, namely, those of Bottone, Robin, Derihon, Saniter, and (to the minimum extent) Stanton.

**Indentation Methods.**—In the **Brinell apparatus** the indenting tool is a spherical ball. If  $P$  be the pressure in kilograms,  $D$  the diameter of the ball in millimetres,  $d$  the diameter, and  $h$  the depth of the indentation also in millimetres, then

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<sup>1</sup> *Amer. Journ. of Science*, 1897, 4, 399.

$$h = \frac{1}{2}(D - \sqrt{D^2 - d^2}) \text{ millimetres,}$$

and the area of the spherical surface of the indentation is

$$A = \pi D h = 1.571 D (D - \sqrt{D^2 - d^2}) \text{ square millimetres.}$$

Then the Brinell hardness is

$$H = P/A.$$

The load  $P$  is known and either  $h$  or  $d$  is measured,  $d$  being the more readily measurable by means of a micrometer microscope.

In the original method described in the year 1900 by Brinell, the area of the spherical indentation was determined by measuring the diameter of the depression. This gave erroneous results, however, as cast iron and Bessemer steel both form ridges around the sphere under the pressure, owing to the metal flowing up from beneath the ball. On the other hand, certain alloys, such as vanadium-copper and Tobin bronze, form an annular depression or negative ridge around the edge. As an intermediate case, moreover, manganese steel behaves correctly, forming no ridge or annulus; but many other alloys behave irregularly. Hence, it has been found that the only trustworthy method of determining the radius of curvature of the Brinell depression is to measure the depth to which the ball penetrates, the  $h$  of the two first equations above given.

One of the best Brinell machines now in current use is that shown in Fig. 436.

It is essentially a hydraulic press, in the heavy base of which the hydraulic power is provided, the liquid contained being glycerine;

the power is produced by the rotation of the wheel seen in front, which is the head of a screw terminating inside in a plunger, the insertion of which by the screw movement invokes the pressure in the glycerine content. From the back of the base arises an upright stout column, which is bent forwards above so as to carry the vertical hydraulic piston, at the lower end of which is the hardened steel ball one centimetre in diameter, which delivers the test. Arising also from the base, directly under the piston,

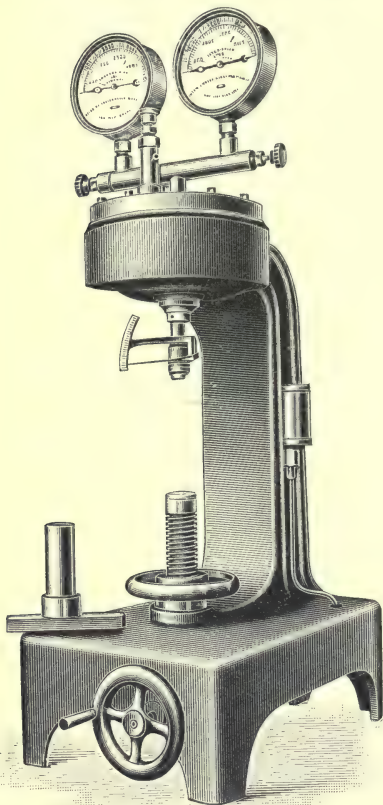


FIG. 436.—Brinell Hardness Tester.

is the testing stage, on which the piece of metal or metallic crystal or other object undergoing the hardness test is to be placed. It can be raised or lowered, to accommodate different-sized objects, and the stage itself is formed by a small steel disc ground spherical on the lower side, which fits into a corresponding spherical depression in the spindle top. An extra piece can be added to lengthen the spindle when small samples are being tested, the extra piece being seen in the illustration lying on the left front corner of the base. The hemispherical levelling stage is removed from its usual position and fitted into the top of the extra piece, when the latter is used. Two pressure gauges are provided at the summit of the instrument. A glycerine seal or trap behind the plunger, partly seen at the right side of the apparatus, prevents any leakage of air into the press during compression.

For measuring the depth of the depression produced in the test a special form of depth gauge is employed, which is attached at the lower end of the piston, and is shown separately on a larger scale in Fig. 437.

This gauge magnifies the distance the ball penetrates 50 times. It is graduated directly in hundredths of a millimetre, the total scale of 150 parts representing an indentation of 1.5 millimetres. It is not affected by shift of the object under

compression or by any "spring" of the whole machine, any such movement being compensated for by a universal joint by which the lower ring is connected to the gauge. It measures, therefore, only the true depth of the indentation produced by the ball in the piece of metal or other object undergoing the hardness test.

To make a test, the sample is placed on the levelling stage, which is then raised by rotation of the wheel seen just above the base at the foot of the spindle, until the object just touches the ball. The indicator arm of the depth gauge should then be adjusted to read exactly 0. The spot on which the ball is to descend should be flat, but the flattened part need not be more than one centimetre in diameter. The pressure may then be applied by turning slowly the plunger wheel on the left (front) of the base in the clockwise direction, until the pressure gauge indicates the desired pressure, 3000 kilograms being a suitable pressure for a hard steel, for instance, but only 500 kilos if the metal or other object be soft.

Obviously this instrument is rarely suitable for use with crystals, large single crystals of a metal, or of a mineral of similar hardness, and which can be got in large crystals, alone being really suitable as regards

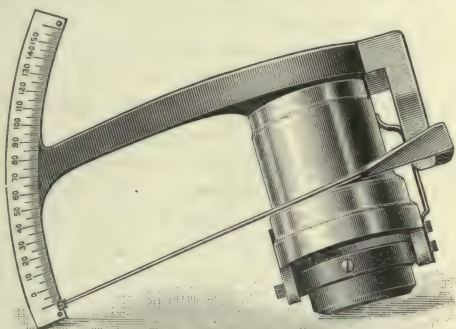


FIG. 437.—Depth Gauge of Brinell Hardness Tester.



the determination of crystal hardness. For metals, however, it is of the greatest use, and of daily application in the engineering laboratory.

The **Shore scleroscope** is a rebound instrument, the essential part of which, the indentation tool, is a diamond-faced hammer, a short cylindrical rod (about  $\frac{3}{4}$  inch long) which is allowed to drop down a glass tube, in which it slides just freely, on the material to be tested from a fixed height, and the height to which it rebounds up the tube is measured by means of a finely graduated scale engraved on the tube. The hammer is lifted and released by air pressure from an indiarubber bulb. The indentating end of the hammer is convex but very small (minimum  $\frac{1}{2500}$  inch). The scale is divided into 140 equal parts, and is such that a moderately hard steel registers 100. The Brinell hardness number is about six times that of the Shore scleroscope. The method is the less satisfactory on account of the fact that the presence of alloying elements which contribute toughness materially affect the amount of rebound, toughness registering as if it were hardness. For example, bronze composed of 90 *per cent.* of copper and 10 *per cent.* of tin gives greater rebound than hard tool-steel.

**Resistance-to-Wear Methods.**—The method of Bottone consists in rotating a soft iron disc at a constant speed and pressure against the material tested, the time required to produce a cut of definite depth being taken as the measure of the resistance.

In Derihon's machine a lever presses the specimen on the circumference of a polished wheel rotating at high speed in an oil bath. The wear is measured in thousandths of a millimetre.

E. H. Saniter in the year 1912 devised a machine for producing wear by dry-rolling friction, a revolving test piece driving by friction on its top side the inner ring of a loaded ball bearing. A member of the Hardness Tests Research Committee, Dr. T. E. Stanton of the National Physical Laboratory, in 1916 improved the Saniter method, and rendered it one of sliding abrasion, by connecting the abrading ring (of internal diameter  $D$ ) to the chuck by means of an Oldham coupling, so that both ring and specimen (of diameter  $d$ ) should complete a revolution in the same time, the line of contact remaining fixed relative to the machine. The slip of the ring over the specimen is then  $\pi(D - d)$  per revolution. The device works well up to a certain load, when "seizing" commences, and the experiments are carried out for loads below this undesirable limit. The abraded particles are removed as fast as they are produced, and rise of temperature prevented, by means of an air blast. The advantage of this method over the rolling-abrasion method is that it does not cause any perceptible hardening of the surface under wear as the experiment proceeds, so that the test is not made on deformed material, as is the case with, and the weak point of, all indentation tests.

Further details of these experiments on Hardness Tests as applied to industrial and armament metals and alloys will be found in the *Report of the Hardness Tests Research Committee*, published by the Institution of Mechanical Engineers in November 1916. Although they are not of direct application to the determination of Crystal Hardness, their

principles and main results should prove of value in guiding towards any further development of the experimental determination of the hardness of crystals, especially as indicating the principles which introduce the undesirable deformation to the least extent.

**Crystal Viscosity and the remarkable Properties of Ice Crystals.**—The occurrence of gliding of the structural units along “glide planes,” described earlier in this chapter (page 531), involving the rotation of the crystal particles or structural units, may be described as catastrophic; for it was shown that a certain critical amount of force had to be exceeded in order to bring it about, greater than the force required for mere temporary elastic deformation. But there is another kind of permanent deformation to which the softer crystals and solids in general are subject, namely, that due to their intrinsic viscosity. Viscosity is the property of undergoing continuous and permanent deformation under the action of a stress, whether the latter be great or small, and with such regularity that the rate of yielding is directly proportional to the stress. The property is well illustrated in the case of ice crystals, and as there are also many other specially interesting features connected with the crystallisation of water, which are both connected with the subject of viscosity and that of glide planes, and are in any case worthy of description as being more or less unique, some of the more essential details concerning ice will now be given.

The crystals of water,  $\text{H}_2\text{O}$ , which we know as ice, have formed the subject of innumerable researches, owing to the many exceptional properties of this solid form of water, and their immense importance to natural phenomena, in the movement of glaciers, for instance, in the floating of ice crystals on water instead of crystal growth at the bottom of the liquid (which only occurs when the bed in which the water lies is colder than  $0^\circ\text{C}.$ , as when “ground-ice” is formed), and in the great force of the expansion which occurs on the solidification of water.

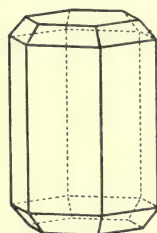
The crystals of ice were long thought to be of hexagonal symmetry, but von Groth, summarising the work carried out on the substance up to the year 1906 (*Chemische Krystallographie*, vol. i. p. 66), considered that in all probability ice belonged to class 20, the ditrigonal-pyramidal class of the trigonal system. Still more recently, however, F. Rinne, in 1917 (see Chapter XXXIII.), has adduced important evidence from X-ray analysis that ice is really hexagonal, its class being 25, hexagonal bipyramidal, and its axial ratio  $a : c = 1 : 1.678$ . A. St. John<sup>1</sup> confirms this, and states that the structure contains four interpenetrating trigonal (triangular prism) lattices (this space-lattice, No. 6, being common to both the hexagonal and trigonal systems), with spacings :

$$\begin{aligned} a &= 4.74 \times 10^{-8} \text{ cm. ;} \\ c &= h = 6.65 \times 10^{-8} \text{ cm. ;} \\ d_{11\bar{2}0} &= 3.79 \times 10^{-8} \text{ cm. ;} \\ d_{10\bar{1}0} &= 2.37 \times 10^{-8} \text{ cm. ;} \\ d_{0001} &= 3.32 \times 10^{-8} \text{ cm.} \end{aligned}$$

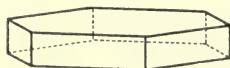
<sup>1</sup> *Nat. Acad. Sci. Proc.*, 4, 1918, p. 193.



The chief form observed consists of hexagonal plates parallel to the basal plane, as shown at *b* in Fig. 438, with edge-faces rarely measurably perfect; sometimes they are found in ice-holes in very large individual crystals, some of which are well-formed hexagonal prisms with basal plane and pyramid faces as shown at *a* in Fig. 438. In cirrus clouds,



(a)



(b)

FIG. 438.—Forms of individual Ice Crystals.

however, ice crystals take the form of thin hexagonal prisms. Sea or lake ice is usually composed of crystals in close contact, and therefore with indeterminate edges, but all having the basal plane parallel to the water surface, the principal (singular) axis being thus perpendicular to the surface; they all, there-

fore, show the uniaxial interference figure, of black cross and circular spectrum rings, in convergent polarised light. The thermal conductivity of ice was found long ago by Forbes to be greatest along the principal axis, and least in directions perpendicular thereto. H. T. Barnes has proved this absolutely in calorimetric experiments in which long needles of ice, exquisite elongated hexagonal prisms, were produced precisely parallel to the lines of flow of the heat. In hail combinations of rhombohedra are recorded, although if Rinne be correct these must really be hexagonal pyramids; hexagonal prisms are common in hail. Snow consists of six-rayed stellate forms, often of great variety and beauty. Two varieties are

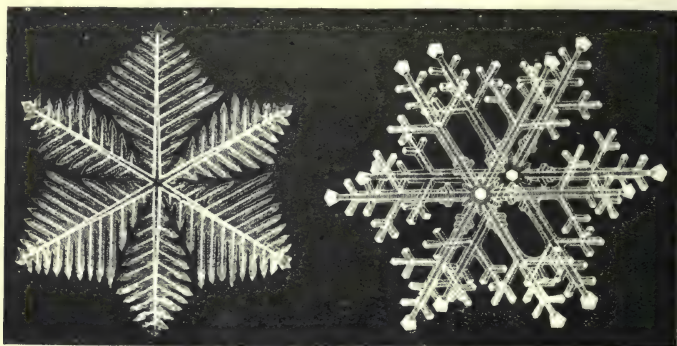


FIG. 439.—Snow Crystals.

represented in Fig. 439 (from drawings by Glaisher). Such snow crystals are usually formed in moderate weather, with light winds or in low clouds, conditions which appear to favour the feathery forms. When the cold is more severe, or the formation occurs in high clouds, the crystals are usually hexagonal columns or solid hexagonal tables of the character illustrated in Fig. 438.

The feathery frost patterns and fern-frond crystallisations on window-



panes, and the wonderful variety of arborescent forms of hoar frost, are familiar to all. A remarkable collection of these forms of ice and snow has been published in the *United States Monthly Weather Review for 1908*, vol. 35, by W. A. Bentley, and republished under the title *Studies of Frost and Ice Crystals*. Two of the most beautiful of the feathery and branching frost-growths are reproduced in Fig. 440.

The manifold beautiful forms assumed by snow and ice are particularly well seen in the Alps, especially in the winter. They have been investigated by many observers, and lately by L. Leigh Fermor.<sup>1</sup> The snow-fields do not remain as when freshly formed, but are subject to constant change. In the early morning hours the snow surface is dry, crystalline, and loosely coherent, the white snow crystals sparkling in the low sun like myriads

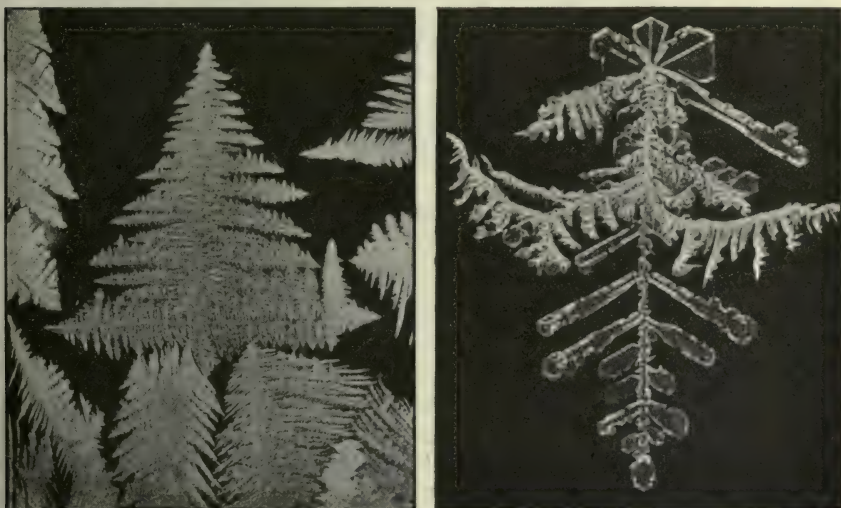


FIG. 440.—Two typical arborescent Frost-growths.

of diamonds. Towards mid-day and in the afternoon, even though it be winter and the air temperature below freezing-point, the sun's heat rays melt the surface snow. As the sun declines, the water wetting the snow crystals or granules begins to freeze again, and by next morning the surface has become rejuvenated with a wondrous growth of ice crystals, most commonly with fern-like forms, built on a hexagonal basis but developed in three dimensions.

A remarkable form found in large numbers by Fermor, the entire surface in shady places consisting of a *cheval de frise* of such, takes the shape of a small hollow hexagonal prismatic spiral, a thin sheet of ice coiled hexagonally around an axis, the faces being parallel to those of the regular hexagonal prism. Fig. 441 is reproduced from the memoir, and will render the structure clear. The prisms were usually from a quarter to

<sup>1</sup> *Min. Mag.*, 1914, 17, 150.

three-quarters of an inch long, and one-eighth of an inch in diameter. Fermor concludes that both the prismatic and the fern-like growths are largely due to abstraction of moisture from the atmosphere. The hollow prisms are more nearly related to hoar frost than to crystals of newly fallen snow.

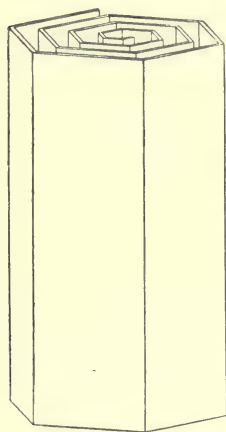


FIG. 441.—Hexagonal Spiral Ice Crystal.

Another interesting form is that of the hollow pyramidal ice crystals described by K. Grossmann and J. Lomas.<sup>1</sup> They consist of hollow hexagonal pyramidal hoppers (inverted pyramids) attached by their points, with the wide-open ends pointing into the air. They also observed a single or double pyramidal spiral arrangement, the latter resembling the helix of an Ionic capital. They were not true spiral pyramids, however, but each triangular face was built up of a stepped alternation of faces of the hexagonal prism with the basal pinakoid. They are thus the same form, pyramidally developed, as that observed in the hollow spiral prisms by Fermor.

When the heat rays from an electric lantern are allowed to pass through a slab of lake ice, the surface of which is focussed on the screen, they cause the ice to begin to melt in numerous spots in the interior of the slab, and the crystalline structure is thereby, as it were, taken down in the inverse order of its formation, with production of cavities (negative crystals) exhibiting hexagonal structure, the celebrated "water flowers." The appearance of these hexagonal stars on the screen is reproduced in Fig. 442, and it will be observed that each star has a bubble at the centre. This bubble is a vacuole except for the presence of water vapour, and the rest of the star-shaped figure or cavity is filled with water. This beautiful phenomenon affords a remarkable demonstration of one of the most important of the exceptional properties of ice, namely, the fact that liquid water occupies less volume than the solid ice which affords it by melting.

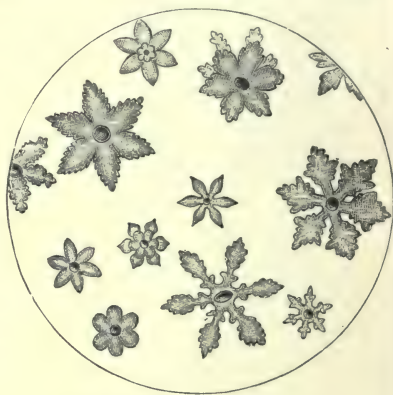


FIG. 442.—Water Flowers.

The peculiar behaviour on the cooling of water begins at  $4^{\circ}\text{C.}$ , when water possesses its maximum density; immediately on cooling below this temperature (down to which the usual contraction of a cooling liquid has been occurring) expansion commences, and proceeds while the water still remains liquid down as far as  $0^{\circ}\text{C.}$  ( $32^{\circ}\text{Fahr.}$ ), when, at the moment of crystallisation into ice, the mass suddenly expands by one-tenth of its

<sup>1</sup> *Nature*, 1894, 50, 600.

volume. The density of ice at  $0^{\circ}\text{C}$ . is 0.9169 compared with water at  $4^{\circ}\text{C}$ . This value is that given by H. T. Barnes<sup>1</sup> as the mean of the many determinations of especial accuracy which have been made by numerous observers. It is obvious that this phenomenon is of vast importance, as ice in consequence floats on water, and in the freezing of rivers, lakes, and even the margins of oceans in the polar regions, the total freezing of the mass of water is prevented or greatly retarded by the surface layer of ice first formed, so that the fish life below the surface is little interfered with. The vacuole in the centre of the ice flowers represented in Fig. 442 is thus the expression of this fact of the immense relative expansion of water on freezing, and contraction of ice on liquefying. We are only too familiar with the great force developed by this expansion when the water freezes in a confined space, such as a pipe or conduit, by the frequent bursting of domestic water-pipes during a keen winter frost. The strength of surface ice is also remarkable, being such that when it is  $1\frac{1}{2}$  inches thick it will support a man; when it is 5 inches thick it will support cavalry and guns; when 6 inches thick it will support horse wagons, and when 18 inches thick it will support a railway train. According to Hess the tensile strength of ice is  $7\frac{1}{2}$  kilograms per square centimetre, and its compressibility 25 kilos. The crushing strength has been given by different observers as from 300 to 1000 pounds per square inch.

The refractive indices of ice as determined by Pulfrich are as under :

Light.	$\omega$ .	$\epsilon$ .
Li	1.3067	1.3080
C	1.3072	1.3086
Na	1.3091	1.3104
Tl	1.3110	1.3124
F	1.3134	1.3147

The double refraction of ice is thus very small, the difference between  $\omega$  and  $\epsilon$  being only 0.0013. Hence a thick slab of ice is required to show a clear uniaxial figure with several rings in convergent polarised light. The refractive index of water is 1.3334 for sodium light and  $20^{\circ}\text{C}$ ., greater than that of ice.

*Glacier Ice* — the consolidated result of the snow falling above the snow-line on high mountains, its accumulation (forming the *névé* or upper snow-fields), and compression into solid ice as it begins to move down the slopes into the natural valleys — is a sort of conglomerate formed of glacier grains, differing, however, from the ordinary geological conglomerate in that there is no matrix but the grains of ice only, fitting perfectly into each other with practically no interspaces between them. Each grain is composed of one or more crystals, and if more than one be present all the crystals are arranged parallelwise, the optic axis being similarly orientated in each and the whole thus behaving as a single crystal. But adjacent grains are not optically parallel, the direction of the optic axis in the different grains varying to any extent. The bounding surfaces of the grains are in close contact, and often interlocked; they are of great importance in connection with the movement of glaciers, as will presently be explained.

Two theories have been put forward to account for the flow of glaciers, the theory of *regelation* and the theory of *viscous flow*. It will be shown in the sequel that while

<sup>1</sup> *Trans. Roy. Soc. Canada*, 1910, 3, 6.



the movement is primarily due to viscous flow, regelation does assist by coming into play at the surfaces of contact of the grains.

"Regelation" is the property which ice possesses of melting under pressure and resolidifying when the pressure is removed, the water formed being in contact with the adjacent ice which had not been under pressure. It is well illustrated by the experiment of placing a thick bar of ice over two supports, one near each end, and suspending a heavy weight from a loop of wire passed around the bar, over the top of the middle of the bar. The pressure immediately under the wire liquefies the ice at the spot, as water at  $0^{\circ}$  C. occupies only  $\frac{9}{10}$ ths of the volume of ice at that same temperature, and the wire, therefore, sinks gradually through the ice bar. For compression of a solid which has formed from its liquid state with expansion was shown by James Thomson in 1849 to cause lowering of the melting-point. But the liberated water freezes again behind the wire, as it is released from the pressure and is in contact with ice all around it; for the melting of the ice had absorbed heat, the latent heat of fusion, lowering the temperature of the water below  $0^{\circ}$ . Eventually the wire passes completely through the ice bar, and the weight with the attached wire falls heavily to the ground or table. The bar remains solid and uncut, however, owing to this refreezing or "regelation," as it is termed. A weal is usually visible afterwards, as a record of the passage of the wire.

Viscosity—the property possessed by a body which causes it to undergo permanent and continuous change of form under the action of a stress, however small, the rate of yielding being directly proportional to the stress—differs from plasticity in that a plastic body requires a definite and increasing stress to produce any and continuous change of form. Viscosity, indeed, is a definite physical constant, and its standard as expressed in the usual C.G.S. units is known as a "poise," in honour of Poiseuille, who first demonstrated that when a liquid flows through a capillary tube of considerable length, at constant temperature, the viscosity is constant at all rates of shear, provided the flow be not turbulent.

The downward movement of a glacier is due to its weight and its viscosity, assisted, as above stated, by regelation at the grain surfaces. The viscosity of a glacier is enormous, vastly greater even than that of a single ice crystal (which is only viscous in the plane perpendicular to the optic axis, whereas a mass of glacier ice is viscous in all directions). The rate of movement, slope, and thickness of a glacier are accurately measurable; but there are two uncertain factors also to be considered, namely, thrust and amount of slip at the boundaries of the glacier. The rate of flow of the Mer de Glace near the Montanvert was measured by Tyndall in July of the year 1857, and again at Christmas of 1859. A straight line of stakes was placed right across the glacier, and it was found that in the course of a few hours the straight line became a curve. Above Trélaporte the glacier is crevassed right across (the crevasses being doubtless largely first formed in the seracs of the ice-fall of the Glacier du Géant, well above Trélaporte), and rock debris falls into the crevasses; by the solar melting of the surface ice these "dirt bands" become visible lower down the glacier (owing to the downward movement of the glacier) as parabolic curves stretching entirely across the glacier. A photograph of these dirt bands, taken by the author in the year 1898, from a point of view well known to climbers as the "stone man," is reproduced in Fig. 443.

This is precisely what would be expected from the laws of viscous flow, assuming ice to be a viscous substance, and the glacier to have a fairly symmetrical bed; for the ice would move faster in the middle and slower at the sides. The exact nature of the movement is stated by Tyndall as follows (page 77 of his *Forms of Water*): "When a glacier moves through a sinuous valley, the locus of the point of maximum motion does not coincide with the centre of the glacier, but, on the contrary, always lies on the convex side of the central line. The locus is, therefore, a curved line more deeply sinuous than the valley itself, and crosses the axis of the glacier at each point

of contrary flexure. Substituting the word river for glacier, this law is also true." He found the winter motion of the Mer de Glace to be only half that occurring in summer.

Tyndall, however, made the mistake of contending that ice would not yield to tension, and was consequently not viscous, founding his conclusion on the supposition that glaciers always crack when subjected to tensile stress. In 1888, however, Dr. Main showed that a bar of ice does yield to tension without fracture, at several degrees below freezing-point, the viscosity becoming greater as the temperature becomes lower; and that the cube of the friction of the sliding ice molecules varies as the square of the velocity. In 1888 also McConnell and Kidd<sup>1</sup> confirmed that ice yields to tension; they showed further that it also yields to compression, but that the direction in the ice



FIG. 443.—Dirt Bands of the Mer de Glace.

is of material importance. They found that a bar of ice cut from a single crystal, so that the optic axis is perpendicular to the length of the bar, does not yield to tension, and it is probable that Tyndall had used such a bar. When the bar was cut, moreover, so that the optic axis was parallel to the length of the bar, the latter only yielded slightly. But when the bar was cut at  $45^\circ$  to the axis it lengthened considerably and continuously, the yielding occurring at right angles to the axis.

In 1891 McConnell<sup>2</sup> found that an ice crystal is easily sheared without fracture along planes at right angles to the optic axis, but in no other direction. The bending of a bar of ice was found to occur by the sliding of a number of planes of finite thickness having this orientation. Such a shear along parallel planes is thus akin to the yield of calcite along its parallel glide planes.

This result finally disproved the views that glacier ice is only plastic under pressure (when liquefaction followed by regelation would occur) and not under tension, and that regelation is the only factor in the process concerned in the movement of glaciers.

In 1895 Deeley<sup>3</sup> showed that the details of glacier flow resemble in every particular the flow of liquids through capillary tubes, and that Poiseuille's equations for such flow can be validly applied to glaciers. These equations are:

<sup>1</sup> *Proc. Roy. Soc.*, A, 1888, 44, 331.

<sup>2</sup> *Proc. Roy. Soc.*, A, 1891, 49, 323.

<sup>3</sup> The work of R. M. Deeley is best given in the following two papers: *Proc. Roy. Soc.*, A, 1908, 81, 250, and *Phil. Mag.*, 1913, 26, 85. There is also an interesting earlier paper by R. M. Deeley and G. Fletcher, *Geol. Mag.*, 1895, 2, 152.



$$\text{Maximum velocity} = \frac{Pb^2}{2\eta}, \text{ and}$$

$$\text{Volume passing any cross-section in unit time} = \frac{Pb^3a}{3\eta};$$

where  $P$  is the force producing the motion (being the exponent of gravity in the direction of the movement, equal in the case of glacier ice to gravity  $\times$  density  $\times$  gradient of glacier),  $b$  is the thickness of the viscous body,  $\eta$  its viscosity, and  $a$  the width of the cross-section.

Deeley further proved the very important fact that, besides the shearing freely of the ice-crystal granules along planes at right angles to the optic axis, they undergo changes at their bounding surfaces of contact, which enable or cause the mass to suffer continuous distortion under stress. Thus the viscosity of glacier ice is not merely that of a single ice crystal, due to shear in the granules, but is also due to interfacial (intergranular) movement. For although the glacier-ice grains can be deformed by a stress producing shear perpendicular to the axis, yet as the grains have their optic axes promiscuously orientated, and the grains moreover interlock one another, the effect of the regular crystallographic glide-plane sliding is largely nullified, and the observed movement of the glacier must be due mainly to another cause which produces the greater portion of the observed viscosity. This other cause is undoubtedly the liquefaction and regelation which occurs at the intergranular bounding surfaces of the ice grains, when molecules of  $\text{H}_2\text{O}$  pass from crystal to crystal, in a manner similar to that which occurs, and causes grain growth, in metals (see Chapter XLIII.).

In view of this further fact of movement at the grain surfaces it is of great interest to determine the viscosity of an individual ice crystal, that is, the true viscosity of the crystallised solid form of the oxide of hydrogen,  $\text{H}_2\text{O}$ , and also to determine and compare with this true viscosity of ice the viscosity of glacier ice. These determinations and comparisons have fortunately been made.

The viscosity of a single crystal of ice perpendicular to the optic axis, the direction in which gliding occurs, was found by Deeley to be  $\eta = 1 \times 10^{10}$  poises. In a later experiment at the freezing-point he found it to be double this, namely,  $\eta = 2 \times 10^{10}$ . It was found that when the weight was taken off the ice bar, in addition to the purely elastic rise, it recovered slowly some of the bending which the weight had produced; most solids do this, although not to so relatively large an extent, and so also does pitch. For viscous substances require time after the application of a stress, in order to afford an accurate permanent result, that is, for the rate of shear to be proportional to the stress, the slow recovery ceasing after a short time. In this respect also a single crystal of ice behaves as a truly viscous crystalline solid, the shear perpendicular to the optic axis obeying very closely the laws of viscous flow. It is as if the crystal were liquid in the plane perpendicular to the optic axis.

As regards glacier ice, Deeley in 1908 calculated the viscosity of the ice of the Mer de Glace, and of the Morteratsch, Lower Grindelwald, and Great Aletsch glaciers. The mean result was the relatively immense viscosity of  $\eta = 7890 \times 10^{10}$  poises. In confirmation, a recalculation of the viscosity of glacier ice from McConnell and Kidd's experiments gave a mean value of  $\eta = 8450 \times 10^{10}$  poises. Deeley considers, however, that the results derived from the Great Aletsch glacier are most trustworthy, owing to the regularity of the slope and the great length of the ice stream. From his latest work on this glacier he finally arrives at the result that the viscosity  $\eta$  of glacier ice in summer is no less than  $12,500 \times 10^{10}$  poises, and that in winter it is probably double this value, owing to the lower temperature.

The movement of a glacier is somewhat faster in summer than in winter, twice as fast (as already mentioned) according to Tyndall, in the case of the Mer de Glace, owing to the glacier being dry and covered with snow in winter. Later measurements



in the case of the Hintereis glacier gave the results of 42 metres per annum in winter and 55 metres in summer, the mean rate per annum being 48 metres.

Thus the most accurate determinations show that the viscosity of a single crystal of ice at the freezing-point is  $2 \times 10^{10}$  poises, while that of glacier ice is  $12,500 \times 10^{10}$  poises, or 6250 times as much. The great difference shows how little of the movement of a glacier can be due to the ordinary crystallographic gliding shear of ice crystals perpendicular to the optic axis, the interlocking and promiscuous arrangement of the single crystal-grains preventing such an effect from being possible on any considerable scale. The observed viscosity, in fact, must be largely due to the intergranular, grain-bounding surface change, of the nature of liquefaction, subsequent regelation and the passage of molecules of  $H_2O$  from grain to grain.

It would thus appear from the great mass of research now accumulated concerning glacier ice and individual ice crystals that while viscous flow is the cause of the movement of glaciers, the viscosity is but slightly due to the gliding shear perpendicular to the optic axis which characterises a single ice crystal, but is due rather to intergranular surface movement, in which regelation plays its natural part. Thus in a sense, very different from that in which it was meant by the older observers, Tyndall for instance, regelation is shown to be a factor in the movement of glaciers, and, like so many other long-drawn-out scientific controversies, that concerning glacier motion has ended in both the rival views contributing their quota to the truth, which is shown to be a blending of the two; the later discovered connecting facts have clearly indicated the exact sense in which each is correct, while the erroneous misconceptions have been eliminated.

**The Foam-Cell Hypothesis and its Application to Ice.**—Prof. G. Quincke has put forward an interesting theory of crystallisation known as the "Foam-Cell Theory." It was suggested by the results of a study of colloidal mixtures, such as silicic acid and glue, which on evaporation form gelatinous masses or thin films, and develop fissures showing considerable regularity. It was found that these viscous films of more concentrated solution exist in a weaker solution of the same substance, and form folds, tubes both straight and twisted, cylinders, cones, spheres, and bubbles, which Quincke considered as either open or closed "foam-cells." The mutual inclination of the foam-cell walls, and their surface tension, were found to change continuously with the concentration.

When three foam walls meet one another the angle between them is  $120^\circ$ . But where a foam wall meets a solid surface the angle is  $90^\circ$ . Hence, angles of  $120^\circ$  are produced if three foam walls meet while still liquid, and angles of  $90^\circ$  when liquid foam walls meet a foam wall which has already solidified. Foams have a tendency to become coarser in structure, the cells growing in size, small cells coalescing to form large ones.

Benzene, when a small quantity is shaken up in a flask and then frozen, forms excellent foam-cells with walls meeting at  $120^\circ$ . Foam-cells are also easily produced by agitating benzene with a strong solution of potash soap (ordinary "soft soap"); in this case, however, the soap solution forms the cell walls and drops of benzene the cell contents. The form of the cells is similar to that of Plateau's froth-cells, in which also the walls are of soap solution and the contents are of air.

The study of the above phenomena led Quincke to the conclusion that the first step to crystallisation occurs in the liquid state, and consists in the segregation, from the solution, of the pure substance hitherto dissolved in the solvent, and the throwing out of any "eutectic" (from  $\epsilon\upsilon$ , "easily," and  $\tau\eta\kappa\omega$ , "I melt," thus meaning literally something readily melted) which may be present. A eutectic mixture is the most fusible mixture of two substances, and it is that particular mixture (as regards proportion) of two crystallisable solids which solidifies *en masse* at a more or less definite temperature, the two sorts of crystals being irregularly interspersed and simultaneously and almost inseparably crystallised together. Under the microscope, however, the two separate substances are readily detected by their different crystals, so that there can be no question of any chemical combination. The so-called cryohydrates of Guthrie, for instance, were eutectic mixtures of ice and salt, containing 23.6 *per cent.* of NaCl, and freezing together at the eutectic temperature of  $-23^{\circ}$  C. The solubility and freezing curves exhibit a sharp change of direction at this point, the "eutectic point," which thus forms the corner of an acute or, at any rate, sharp angle in the curve. Similarly, the freezing-point curve for solutions of carbon in molten iron shows a sharp change at the eutectic point, which corresponds to 4.3 *per cent.* of carbon in the iron and occurs at  $1130^{\circ}$  C., so that at the slightest fall in temperature the whole of such a mixture solidifies *en masse*.

Quincke then considered that in the two liquids separated as above described, pure substance and eutectic, differences of cohesion cause the pure substance to aggregate in spheroidal masses, around which the eutectic forms in bubbles, "foam-cells." These spheroids of pure substance, being isolated from each other by the foam-cell walls, within which they are confined as cell-contents, are thus free to develop each their own crystalline orientation. This may occur while they are still liquid, or only on solidification, but in either case the result is the same, namely, the solidification of each spheroid as a little sac of uniformly, parallelwise, orientated molecules or polymolecular crystal-structural-units. The orientation of the crystal-contents of adjacent foam-cells, however, is promiscuously different.

In applying this theory to ice, Quincke supposes that the individual crystals of ice are the pure  $\text{H}_2\text{O}$  contents of foam-cell films, the substance of the films themselves being water containing the impurities, salts in solution, such impurities being considerable if it be sea water which is freezing, and less in quantity if the water be fresh or only brackish. He considers this to be proved by the fact that comparisons of the freezing of ice from pure distilled water on the one hand, and from water containing added soluble salts on the other hand, show that in the case of the impure water similar phenomena are observed to those which he had observed with the colloids. Moreover, the breaking up of ice with conchoidal fracture he considers as fracture along the foam-cell walls, which are generally invisible in ordinary light; the fracture occurs owing to these more or less spherical cell walls having contracted differently from their pure  $\text{H}_2\text{O}$  contents.



Glacier grains are immediately explicable by this theory, as simple foam-cells filled with pure ice, the cell-wall films or surfaces of contact of adjacent grains being composed of the aqueous solution of the impurities (soluble salts). As the freezing proceeds, the mother liquor (water containing dissolved salts) continually becomes more concentrated and the foam walls thinner. Finally, these walls also freeze, to ice and solid salt (a eutectic mixture or Guthrie cryohydrate freezing *en masse*). Air, which has been dissolved in the water, also separates in cavities or bubbles, and causes the white places in ice, generally accumulating at the places rich in salt, and often producing tubes normal to the surface of the ice. The more slowly ice is produced, and the less salt it contains, the fewer are the foam-cells, and consequently the larger are the individual crystals, and also the more transparent and rigid it is.

The walls of the foam-cells, that is, the bounding surfaces of contact of the ice-crystal-grains, are more rapidly and readily affected by the sun's heat than the pure ice within the cells (grains), and it is probable that the same occurs in the production of the "water-flowers" (Fig. 442, page 546) by the heat rays from an electric lantern. For the water-flowers appear first at grain boundaries, according to Quincke. It is, therefore, doubtless by the liquefaction of the grain boundary-surfaces by the solar heat rays, and subsequent regelation, that the movement of glaciers, as explained in the previous section, is so materially assisted, and which confers on glacier ice the greater part of its observed viscosity.

**The Pulsation-Cell Theory.**—Another theory of crystallisation has been originated by Sir George Beilby, and is known as the "Pulsation-Cell Theory." The molecule is regarded as spherical in the simpler cases of elementary substances (such as the metals which have formed the prolonged study of the author of the theory), and also as elastic, and its vibrations are assumed to be spherical pulses of enormously rapid period. The effect is to surround the sphere with a "pulsation-cell," the thickness of which depends on the amplitude of the pulsations. As the amplitude depends on the temperature, for each temperature the cell is of definite thickness. The outer surface of the cell, although purely kinematic (the pulsations being in response to heat waves from the ether), forms a real bounding surface. When the heat energy is sufficient to cause volatilisation to the gaseous condition the pulsation-cell-boundary still subsists, and collisions of molecules occur off it as the bounding surface. The packing of cells in the solid state, under the influence of cohesion alone, is not the closest possible; on the contrary, it can be extremely open, and there is no tendency to organised arrangement. A collection of molecular pulsation cells, however, will have the power of self-arrangement. This power will be feeblest with strictly spherical pulses, but becomes a powerful influence when the pulses are predominately equatorial or polar, the cells then becoming oblate or prolate spheroids. These tend to arrange themselves in homogeneous assemblages, in accordance with the laws of crystallography and of the geometrical theory of crystal structure.

When the molecules are complex, consisting of two or more atoms of different kinds, different chemical elements, it will be obvious that the



forms assumed by the pulsation cells will be very various, but definite for the same substance at any particular temperature. As the form and size of the cell depends on the temperature, the theory accounts equally well for the case of polymorphism, as the different crystalline phases are each associated with a definite range of temperature.

**The Viscosity of Crystallised Metals.**—The discussion of the granular structure of ice and its important bearing on the viscosity of ice is of considerable interest relevant to the very similar case of metals. It will be shown in Chapter XLIII. that the structure of most metals, as industrially prepared by solidification from the state of fusion, is usually one either of interlacing closely aggregated individuals (see Fig. 15, page 28), of every possible orientation with respect to each other, or of closely packed crystal grains (see Fig. 713); each grain consists of similarly orientated individuals (if more than one be present in the grain), but adjacent grains are, in general, differently orientated as regards their crystal-symmetry. In annealed and cast metals the grains are roughly of the same order of size, and polyhedral rather than spherical, owing to contact with neighbouring grains. More or less distortion of the grains or “strain-hardening” is brought about by the usual processes employed in the mechanical working of metals. It is now further generally held by metallurgists, particularly by Rosenhain,<sup>1</sup> Beilby, Osmond, Humfrey, and others, that a thin layer of amorphous metal, in a state corresponding to that of a greatly undercooled liquid, exists between adjacent crystals or crystal-grains, acting as a cement, and which is sufficiently mobile to yield to the tendency of any applied stress to produce flow. A flow sufficient to cause rupture, however, only occurs at the crystal boundaries, and when these latter are smooth, tending towards rectilinear polygonal forms (as seen in section in Fig. 713). In the more usual case of truly interlocked or dovetailed boundaries, formed by the growing crystals thrusting out projections into their neighbours, such rupture is impossible, and the flow only occurs as a movement similar to that of glacier ice, which may be considered as viscous flow, the permanent effect of prolonged stress and proportional to the amount of the stress. The rarer case, when the bounding surface-films are smooth, is that which is observed in the phenomenon known as “season cracking.” In this case the parting of the metal actually occurs and follows the intercrystalline boundaries, and does not disrupt or fracture the crystals themselves. It may be due to the prolonged action of small stresses, far below the breaking strength, arising either from externally applied forces or from elastic deformations and consequent internal stresses.

The facts are of considerable industrial importance, as it will be obvious that processes which produce—in iron and steel for instance—a metal which is composed of a microcrystalline aggregate of crystal grains with smooth boundaries are to be avoided, as producing a metal very liable to fracture. Such a process to be avoided is drastic annealing, which allows the crystals to attain a condition of metastable equilibrium in which their outlines have

<sup>1</sup> W. Rosenhain and S. L. Archbutt (*Proc. Roy. Soc., A*, 1919, 96, 55) give a useful summary of the literature on this subject.

had an opportunity of becoming smooth and regular. The operation of "normalising" mild steel, by heating it for a very short time to a temperature just above the upper critical point, followed by rapid cooling in air, is fortunately sufficient to eliminate all risk of the development of these dangerous structural arrangements, liable not only to viscous flow but to absolute failure by fracture along the intercrystalline boundaries. The immunity from numerous and serious failures from this cause is due to the fact that the majority of metals, as ordinarily employed, crystallise in the interlocked and interthrusting condition, not favourable either to viscous flow or to actual intercrystalline fracture. Such safe, strong metal, when broken in the testing machine, exhibits the usual fracture running *across* the crystals and avoiding the crystal boundaries in a systematic manner.

We have here an illustration of the great use of the crystallographic microscopic study of metals, the rapidly growing important subject of Metallography, in discovering the sources of weakness of metals in daily use, and in indicating the means of their prevention and elimination.

**Plasticity of Ammonium Nitrate.**—The needle-like crystals of ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , obtained from aqueous solution at the ordinary temperature, exhibit remarkable plasticity. They can readily be bent and twisted by the fingers, and indeed small loops of half a centimetre diameter can be made of these flexible crystals if the bending be done carefully and slowly. If the bending be sudden and rapid, however, the needle breaks, the crystal being brittle as well as plastic. The crystals are most readily bent when fresh from their mother liquor. The curve of the bent crystal is not a bow like that of an elastic substance, but is almost pointed, V-shaped. The crystals are elongated rhombic prisms, of pseudo-tetragonal habit, usually without end-faces, and with a complex cross-section suggestive of repeated twinning. Yet when the bending occurs no longitudinal slip is observed at the ends, and the inner edge of the crystal is compressed and the outer edge extended, as in elastic bending. The optical characters are but little altered by the bending, the plane of the optic axes remaining parallel to the length of the needle, and the optic axial angle  $2E$  remaining  $59\frac{1}{2}^\circ$ .

Bending experiments carried out by W. N. Bond<sup>1</sup> have shown that the rate of bending is not directly proportional to the stress, but increases rapidly with increase of stress. A slight unbending occurs when the load is removed, showing that the crystal is slightly elastic, but most of the bending is permanent, and is probably plastic in its nature. That the change of form is not due to simple viscous flow is indicated by the fact that there is no unique value for the viscosity. A pseudo-viscosity, calculated as if the bending were viscous, gave results of the same order as those of glacier ice; for the rate of bending is almost the same as that observed by Deeley for glacier ice. The final conclusion of Bond is that a rotation occurs in the atomic groups, of such a nature that the atoms remain in equilibrium in a similar space-lattice at their new distances apart.

<sup>1</sup> *Phil. Mag.*, 1921, 41, 1. For the other three (polymorphous) forms of ammonium nitrate see second paragraph of Chapter LV.

## CHAPTER XXX

### CRYSTALS AS HOMOGENEOUS STRUCTURES

THE geometrical regularity in accordance with a definite plan of symmetry which has been experimentally shown in Part I. to be a characteristic of crystals, the constancy of the interfacial angles, the zonal relationships, and particularly the rationality of intercepts and of facial indices, all unite in compelling us to the conclusion that these interesting phenomena, connected with the exterior shape of crystals, owe their origin to the fact that the material units of which the crystalline substance is composed are themselves arranged in an orderly manner, according to some regular structural plan. In other words, we conclude that a crystal is a homogeneous structure, the essential nature of which is that the arrangement about any one structural unit (in general, the chemical molecule or small group of molecules) is the same as about every other. It will be obvious, therefore, that a knowledge of the nature of all the possible types of homogeneous structures must be of immense importance in enabling us to understand correctly the real nature of crystals.

It will be shown in the next chapter (XXXI.), devoted to the volume relationships of crystals, that we arrive, as the result of the purely practical experimental investigation of crystals, at a system of points, the centres of gravity of the chemical molecules or polymolecular groups, or some particular atom analogously chosen from each molecule or group, as representing the crystal structure. Upon such an assumption the whole of the phenomena can be readily explained, and the relative separation of these points along the axial directions of the crystal can be actually determined for any definitely related series of substances, such as the members of an isomorphous series of salts. Indeed, it appears likely that we may eventually be able to compare these structural dimensions, the separation of the points representing the structural units, for all kinds of substances, even the most diverse in character, with each other. Moreover, it will be shown in Chapter XXXIII. that in the new mode of analysing crystals by X-rays we possess a means, not only of confirming these relative measures of the distances separating the representative points of the structural units along the crystal-axial directions, but of determining those distances in absolute measure in space.

Before passing, therefore, to the systematic discussion of the subject of internal crystal structure, it will be both advisable and interesting to review briefly the great progress which has been made of late years in our knowledge of homogeneous structures in general, especially as this purely geometrical work appears now to be fairly complete.



The important pioneer work of the Abbé Haüy,<sup>1</sup> Professor of the Humanities at the University of Paris, has already been alluded to in Chapter I., in reference to his belief, now proved to be a fact, that difference in chemical composition is accompanied (except in the case of the invariable cubic substances) by difference in crystalline form. The results of his remarkable researches were first communicated to the French Academy and then shortly afterwards, in the year 1784, published in a book entitled *Essai d'une théorie sur la structure des cristaux*, of which the author is in possession of one of the original copies. It is shown therein that all the varieties of crystalline forms can be referred to a few simple types of symmetry, and proofs are offered that all the apparently different forms of the same substance are based on one of these simple fundamental forms. Moreover, Haüy enunciated the laws of symmetry, discovered the law of rational indices, and pointed out the simple relation between crystalline form and cleavage, the latter phenomenon having been discovered four years previously by Bergmann and Gahn. Besides these indubitable facts, which will ever render the name of Haüy famous as the "father of crystallography," he also originated a most interesting theory as to the nature of the fundamental structure of crystals, which was for long discredited, but which is now proved to have a substratum of truth; for he imagined that the ultimate particles, which he called "molécules intégrantes," were the primitive parallelepipeda themselves, which in the most general case were of unequal angles and three dimensions of sides, but gradually became, through the various stages of symmetry, the cube of right angles and equal sides. It is quite conceivable that a solid structure built up of such minute elementary parallelepipeda would develop on its exterior surface only such planes as would be formed by the structure terminating in some regular manner, for instance, by each line of parallelepipeda being longer or shorter than the next one by some

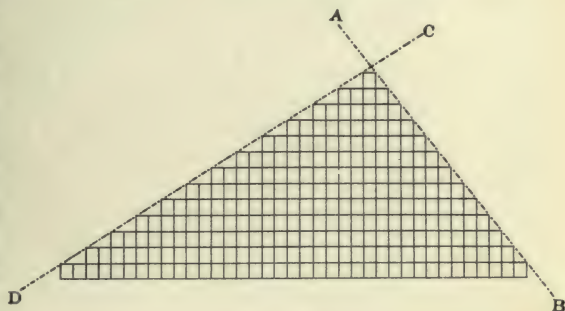


FIG. 444.

small rational number, such as one, two, three, or four parallelepipeda. Thus in Fig. 444 the plane AB is formed by the terminations of either horizontal or vertical lines of parallelepipeda, each of which is one parallelepipedon longer horizontally (passing from A to B) than the preceding

<sup>1</sup> The Abbé René Just Haüy was born in 1743 and died in 1822. On Feb. 28, 1918, an Exhibition of his portraits, MSS., and letters was held at the American Museum of Natural History, New York, in commemoration of the 175th anniversary of his birth, and papers were read in appreciation of his work. An account is given in *Amer. Min.*, 1918, 3, 49.

one, whereas the plane CD is formed by the terminations of similar lines, but each of which is two parallelepipeda longer than the preceding one. It is easy, for instance, to build up a pyramid, which may represent the half of an octahedron, from a large number of small cubes, and grossly mechanical considerations such as these may be of assistance to the mind in grasping some germ of the truth regarding the reason for the formation only of such faces as have rational indices, composed of very small whole numbers.

But the advance of physics has gradually made it clear that the chemical molecules cannot be thus arbitrarily considered as solid parallelepipeda, closely packed without interspaces, for it would then be difficult to account for the well-known molecular movements accompanying elastic compression and thermal expansion and contraction. It is, in fact, certain that solids resemble liquids and gases in consisting of molecules separated by interspaces, now reduced to a minimum, in which their proper movements occur. Instead, therefore, of considering the actual

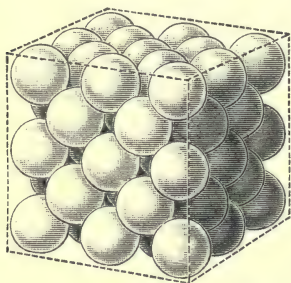


FIG. 445.

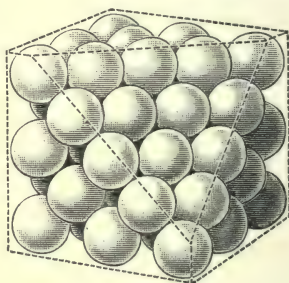


FIG. 446.

shape of the molecule as being that of the primitive parallelepipedon, the idea of shape is eliminated, and the molecule is considered as being replaced by its "sphere of motion or influence," which may be represented graphically by a point, its centre of gravity or mean position about which the motion occurs, or any other point so long as analogous points are chosen in all the molecules. It is just as easy to consider the crystal as built up of spheres as of cubes, as shown in Figs. 445 and 446, and the explanation of rational indices is as simple on the one basis as on the other. The relative distances apart of the representative points are, of course, determined by the intermolecular forces.

We thus come to the same conclusion as that referred to in the second paragraph of this chapter as being derived from a study of the volume relationships, namely, that a **crystal may be considered as an orderly assemblage of points, the centres of gravity or other representative analogous points of the chemical molecules** or of small aggregates of molecules forming the grosser crystal-structural-units. This modernised interpretation of Haüy's idea of "*molécules intégrantes*" is in harmony with all the known facts of morphological crystallography, and offers a rational explanation of the observed types of crystal symmetry and of the law of



rational indices. It is also in full accord with the results of the recent investigation of crystals by means of X-rays.

Fig. 447 represents such an orderly assemblage of points, of the most general character, in which the distances 1 to 2, 1 to 3, and 1 to 4, separating them along the three main axial lines, which we may consider as the lengths of the morphological axes  $a$ ,  $b$ ,  $c$ , are unequal, and the interaxial angles  $\alpha$ ,  $\beta$ ,  $\gamma$  are also unequal. These three axial directions are distinguished by the different kinds of thin lines in the figure, the  $a$  direction being marked by broken lines, the  $b$  direction by broken-and-dotted lines, and the  $c$  direction by continuous lines. If we consider the point 1 as

the origin,  $X\bar{X}$ ,  $Y\bar{Y}$ , and  $Z\bar{Z}$ , drawn in thick broken-and-dotted lines, may be regarded as the axes themselves. But any other of the points may be equally well regarded as the origin. This type of assemblage would correspond to a crystal of the **triclinic** (otherwise called **anorthic**) variety, which possesses no symmetry other than that about the centre. When, however, any two of the interaxial angles, say  $\alpha$  and  $\gamma$ , are right angles, one of the axes, in this case  $b$ , being then perpendicular to the plane containing the other two (which remain inclined to each other in that

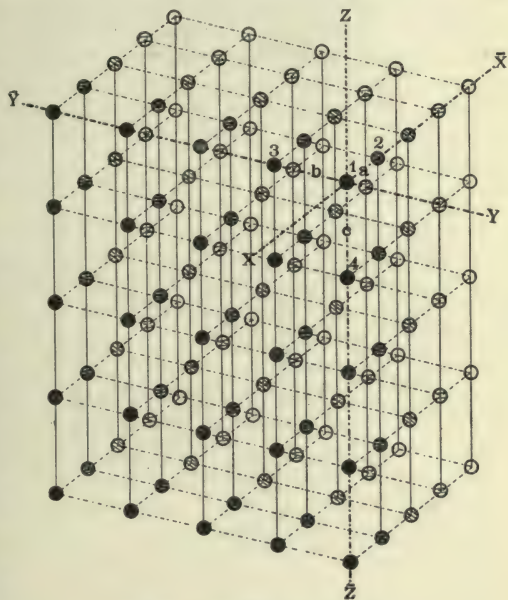


FIG. 447.—Triclinic Space-lattice.

plane), the type becomes that of a **monoclinic** crystal. When all three interaxial angles  $\alpha$ ,  $\beta$ ,  $\gamma$  are right angles, but the distances separating the points along the axial directions (that is, the axial lengths) remain unequal, we have the **orthorhombic** kind of crystal symmetry. When the three angles are all right angles and also two of the axes, conveniently chosen as  $a$  and  $b$ , are of equal length, the symmetry ascends to that of the **tetragonal** order. When, further, all three axes are equal, in addition to being all arranged at right angles to each other, the maximum possible symmetry is attained, known as **cubic**. There are still two more possibilities. For all three axes may be of equal length, and all three angles equal to each other but not right angles; this is the case of **trigonal** symmetry. The other case is similar to that of the tetragonal variety, only that the two equal axes are inclined at  $60^\circ$  instead of  $90^\circ$  to each other; this is the case of **hexagonal** symmetry.



Such a parallel three-dimensional net-like arrangement of points is termed a "**space-lattice**," and its chief characteristic is that the environment about any particular point is the same as about any other, the strictly parallel arrangement of the units represented by the points being at the same time an absolutely essential condition. For it will presently be shown that similar environment alone is a property common to no less than 65 point-systems, of which only 14 are either space-lattices, or can be reduced to such. An actual cubic space-lattice, that of either rock-salt NaCl or sylvine KCl, will be found illustrated in Fig. 540 in Chapter XXXIII.; the solid dots represent the atoms of either sodium or potassium, and the ring-dots those of chlorine, or *vice versa*.

Now a crystal is just such a homogeneous structure—that is, an assemblage in which the environment about every molecular or poly-molecular unit or its representative point is the same as about every other—formed by the symmetrical arrangement of an indefinitely large number of spheres of atomic influence, the cluster of which constituting each molecule or small group of molecules may be considered as represented by a single point of the space-lattice; and it was shown in Chapter IX. that there are seven styles of crystal architecture, or "**systems of symmetry**," corresponding precisely to the seven space-lattices just described.

The proper chemical proportions of the atoms of the different elements present in the molecule are assured in the whole structure by the fact that the latter is of such a character that it may be partitioned into cells identical in composition and configuration with the chemical molecule or small group of molecules (although the individuals forming the group in the cases of polymolecular crystal units are not necessarily arranged parallelwise); for the arrangement of the atomic spheres of influence within the cell is such as corresponds with the stereometric arrangement of the atoms in the molecule, and also, as we shall presently see, with a particular homogeneous arrangement of points representing the constituent atoms themselves which corresponds (together with that of its fellow molecule or molecules in the case of a group) in turn to a specific subdivision or "class" of the system of symmetry.

The problem of the nature of the crystallographic structural units, as to whether we are to consider the chemical molecules or their constituent atoms as such units, is somewhat complicated by the probability already mentioned, that in solid substances we are frequently dealing with edifices composed of units which are aggregates of chemical molecules. Many attempts have been made to determine the number of chemical molecules contained in the so-called physical molecule. But no definite success attended these efforts, as was shown by the author in a memoir on "The Nature of the Structural Unit,"<sup>1</sup> until the discovery in the year 1912 by Laue that the minute (shorter than the distances between the atoms) waves of X-rays are diffracted by the planes of atoms in the space-lattices of crystals, just as the grosser light waves are diffracted by a ruled grating. For in subsequently perfecting this discovery Sir William Bragg and his collaborators have been able to elucidate the nature of

<sup>1</sup> *Journ. Chem. Soc.*, 1896, 69, 507.

the structural units of a considerable number of substances, and found them to be in many cases polymolecular. For instance, at the author's suggestion and with his material, Sir Wm. Bragg took up the X-ray analysis of the isomorphous series of the orthorhombic sulphates and selenates of the alkalis,  $R_2\overset{S}{\text{Se}}\text{O}_4$ , of which our typical crystal substance potassium sulphate is the first member. The actual work was carried out in Sir Wm. Bragg's laboratory by Prof. A. Ogg and Mr. F. Lloyd Hopwood,<sup>1</sup> and they discovered that the crystal unit is composed of four molecules. In the case of the more complicated monoclinic double sulphates and selenates containing the same bases along with dyad metals and six molecules of water of crystallisation,  $R_2M(\overset{S}{\text{Se}}\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ , also investigated by the author, the structural unit of the space-lattice will more probably prove to be simply the chemical molecule, or at most two molecules; but this more difficult case has not yet been analysed by the X-rays. A special chapter will be devoted (Chapter XXXIII.) to this interesting new X-ray analytical method.

It has proved conclusively that the chemical atoms are the ultimate units of crystal structure; for it is the planes of the atoms themselves which reflect the X-rays, and which do so to an extent which differs for the different chemical elements present, when the substance is a chemical compound. The planes of the chemically similar atoms, at any rate those of the dominant element (the metal in a salt, for instance), have usually been clearly indicated as planes of one of the 14 space-lattices, the dimensions of which have actually been afforded.

**Evolution of the Geometrical Theory of Crystal Structure.**—In the year 1830 Hessel made a study of the types of symmetry possible to a solid bounded by plane faces, and then, by excluding all such types as did not fulfil Haüy's law of rational indices, he found that only 32 types were left as possible to crystals, assuming the law to represent a natural truth. At this time, however, comparatively only a few of these 32 classes of crystals had been actually observed, and Hessel's conclusion, published in book form in Leipzig under the title *Krystallonomie und Krystallographie* in 1831, remained unnoticed. The same fact, however, was independently discovered by Gadolin in 1867, and Hessel remained unknown until Sohncke fortunately alighted upon his book so late as 1891. But Gadolin having published his results both in a memoir<sup>2</sup> and in book form at Helsingfors, they were seen and at once taken up. In the previous year Victor von Lang, the well-known mineralogist of Vienna, who for some years was with us in England at the British Museum, had published the first edition of his *Lehrbuch der Krystallographie* (Vienna), in which he had thoroughly laid down the laws of symmetry, and although he did not arrive at all the 32 classes, his method was capable of reaching that result had he carried it to its logical conclusion. In subsequent memoirs and further editions of his book the

<sup>1</sup> *Phil. Mag.*, 1916, 32, 518.

<sup>2</sup> *Acta Soc. Scient. Fennicae*, 1867, 9, 1.



completion was eventually carried out, so that between Gadolin and von Lang the geometry of the symmetry of the 32 classes of crystals, as concerns their exterior configuration, was by the year 1870 thoroughly well established.

As regards the internal structure, the first authentic conception of a crystal as a network of molecular points, quite independent of any shape the molecules may possess, was advanced by Seeber in the year 1824, in a memoir in Gilbert's *Annalen der Physik*, vol. 76, p. 229. The idea was subsequently further developed by Dana in 1836, Brewster in 1839, Delafosse in 1843, and Forster in 1855, and it has since become generally accepted that the grosser crystal structure consists in the similar repetition of the ultimate identically similar molecular or polymolecular units throughout the space occupied by the crystal, without any regard whatsoever to the shape or constitution of these units. At the same time it is true, and will be afterwards proved, as regards the finer details of the structure, that the stereometric arrangement of the chemical atoms in the molecule, and, in the case of polymolecular units, the mutual disposition of the individual molecules in the group, has a profound influence on the choice of the particular one of the 32 crystal classes which a specific chemical compound shall exhibit.

The problem thus simplified by the elimination of the shape of the molecules was to discover the various possible modes of homogeneous repetition of the ultimate parts, that is, to ascertain what types of homogeneous partitioning of space are possible, and then to see if these account for the observed 32 varieties of crystal species.

From this point of view Frankenheim in the year 1842 investigated the possible parallelepipedal networks of points, and came to the conclusion that there are 15 possible different symmetrical arrangements, of the nature of space-lattices, of the ultimate particles in space, the shape of the latter being altogether excluded from consideration. This, however, leaves entirely untouched the so-called hemimorphous and hemihedral classes of crystals, that is, crystal species showing only partially the symmetry of their system or genus, the former (hemimorphous crystals) being differently terminated at the two ends of a principal axis. Now it has been clearly shown in Chapter IX. that these species lacking the full symmetry of their genera are as much forms of definite symmetry as are the seven holohedral forms which display the full symmetry of the seven crystal systems, the seven genera of crystallography. Hence, Frankenheim's proposition was only the beginning of a full and comprehensive theory, which should account for the whole of the 32 class species.

In 1848 Auguste Bravais gave rigid proofs for Frankenheim's space-lattices, and showed that two of the 15 are identical, so that there are only 14 distinct space-lattices, which are fully described in the next chapter (XXXI.). These he assigns to seven systems, according to the number and nature of the axes of symmetry which pass through a given point of the space-lattice, and these seven systems are identical with those into which crystals naturally fall. In his "*Mémoire sur les systèmes formés par les points distribués régulièrement sur un plan ou dans l'espace*"



and "Études cristallographiques,"<sup>1</sup> he not only develops these definite results but goes further by suggesting that the shape of the units represented by the points determines the hemihedral or other forms which only partially represent the symmetry of the system. For the 14 space-lattices are all holohedral (holosymmetric), possessing the full symmetry of the system concerned in each case. He further states that the geometrical arrangement of the constituent atoms is the same round the centre of gravity of each molecule. Thus Bravais stipulates a fixed relationship, same-way orientation, and rigidity of the parts of the molecule, and he considered that the process of crystallisation consisted in the rotation of the molecules in such a way as to bring about this uniform orientation about every molecular centre or point of the space-lattice.

This hypothetical fixed position of the atoms in the molecule of the crystalline solid is now an experimentally proved fact. Its establishment, as regards certain holohedral crystals such as our typical crystal of potassium sulphate, is one of the most interesting results of the author's own investigations, fully confirmed by the results of X-ray analysis.

Bravais also introduced the fruitful conception of a "coincidence movement," a movement by which an assemblage of points is brought again into coincidence with itself, point with point; it is as if there had been two duplicate assemblages in coincident superposition, and one of them had been given a movement of translation or rotation, or both these movements combined, such that when it came to rest all the points of the two assemblages became superposed again, although not so that the same points were in superposition as at first, but so that the appearance was that of one and the same single assemblage only, just as at first. That is, unless one had been told that a movement had occurred one would not have suspected it. This conception has been of inestimable value in the study of symmetry, and is one rich in mathematical results of considerable importance.

The chief work of Bravais is undoubtedly, however, his definite proof of the geometrical existence of the fourteen separate space-lattices, and the explanations which he offers by their means of the experimental law of rational indices, of the homogeneity of the crystal, and of the development in actual fact of seven generic systems of crystal symmetry. For all the fourteen space-lattices have the property of homogeneity in common, their planes of points (each or any plane passing through three of the points, which are adequate to define its position in space) are all possible crystal faces complying with the law of rational indices, and the symmetry of each space-lattice is that of one or other of the seven crystal systems. Indeed the nature of the space-lattice formed by the arrangement of the molecular or polymolecular centres of a crystalline substance, or of any analogous points which may be taken within the molecules or groups of molecules, one from each molecule or group, to represent them instead of their centres of gravity, determines both the crystal system and the obedience of the facial planes developed by the crystal to the law of rational indices. These weighty facts alone would entitle Bravais to a large share

<sup>1</sup> *Journal de l'École polytechnique*, Paris, 1850, 19, 127, and 1851, 20, 102 and 197.

of the honour due to the discoverers of the true theory of the homogeneous partitioning of space.

The next step forward was the enunciation of the principle of the symmetrical repetition in space by Wiener in 1869, in his *Grundzüge der Weltordnung*. Broadly stated it is, that regularity of arrangement of analogous atoms consists in every such atom having the remaining atoms arranged about it in the same manner (although it may not always face the same way). In other words, homogeneity consists primarily in the continual repetition throughout space of the same relation between an elementary atom and the entire structure, regarded as unlimited. Wiener described several specific kinds of regularly symmetrical repetitions of identically similar points in space, as examples of his new principle.

But the exhaustive discussion of such assemblages we owe to a pure mathematician, Camille Jordan, who later in 1869 published a "*Mémoire sur les groupes de mouvements*"<sup>1</sup> in which he defined the possible types of regular repetition in space of so-called identical parts, the term "identical" here meaning more than merely "ordinarily similar," namely, "perfectly alike." He showed that when such identical repetition occurs in a rigid system, a definite group or series of movements may be employed in regard to it, each movement being such that while shifting the system it leaves the appearance the same as before, every point being moved to a position previously occupied by a homologous point. The great advantage of this method is its complete generality, no further limitation being required than that which prescribes the kind of repetition presented by the homologous points of the structure.

It is interesting and somewhat remarkable that Jordan's work was entirely conceived without any reference whatsoever to crystals, a testimony to the value of pure mathematics in paving the way for the explanation of natural phenomena. The method was applied to crystals by Leonhard Sohncke in his *Entwicklung einer Theorie der Krystallstruktur*, Leipzig, 1879, and numerous later memoirs, an especially important one,<sup>2</sup> embodying his maturer ideas, being published in the year 1892. Leaving out of consideration such parts of Jordan's work as were not applicable to crystals, Sohncke showed that when we drop the limitation of the 14 space-lattices of Bravais—that the units are all arranged parallel and similarly orientated to each other—and admit Wiener's principle and Jordan's more general definition of homogeneity (that the arrangement is merely such that the environment about every point of the assemblage is the same as about every other), we at once admit 65 point-systems, that is, we are able to arrange points in space in 65 typical ways. Each of these 65 "Sohncke regular point-systems," except the least symmetrical of them (his No. 1), which has no axes, consists of a homogeneous assemblage of points symmetrically and identically arranged about axes of symmetry, which in some cases are screw axes, so that the points surround them in a spiral manner, the resultant of a rotation and a translation. They consist, in general, of two or more interpenetrating identical space-

<sup>1</sup> *Annali di Matematica*, Milan, [2], 1869, 2, 167.

<sup>2</sup> *Zeitschr. für Kryst.*, 1892, 20, 445.



lattices, and, in fact, the atomic points of a Sohncke system may always be grouped together in molecular or polymolecular sets such that the centres of gravity (or any other representative points analogously taken, one from each molecule or group) of the sets constitute a Bravais space-lattice, which obviously governs the crystal-system to which the crystal shall conform, while the atomic point-system itself determines the particular crystal-class. In certain special cases the Sohncke regular point-system becomes reduced directly to a Bravais space-lattice. Moreover, it is clear also that the law of rational indices must be equally applicable to a Sohncke point-system as to a space-lattice, as the former can be resolved into the latter, or into two or more identical space-lattices.

But this earlier work of Sohncke was not complete, for it did not cover the cases of hemimorphous crystals, those which are differently terminated at the two ends of a prism axis, nor all the cases of enantiomorphous crystals, those the two varieties of which are related as a right and a left hand, mirror-images as it were of each other. To explain these, Sohncke at first resorted to the supplementary hypothesis that molecules are endowed with polarity, an assumption which is unsatisfactory, unnecessary, and now known to be erroneous. As far as his 65 point-systems are concerned, however, Sohncke was on sure ground, and after the next step had been indicated by the other three workers to whom reference must now be made, Sohncke himself was the first to recognise their advance, at any rate as regards the work of Schönflies, and applied it to complete his own method. A complete account of the 65 regular point-systems is given in the latter part of the next Chapter (XXXI.), with a drawing of each, and their mode of distribution among the 32 crystal classes.

The final step in the building up of the geometrical theory of crystal structure affords one of the most remarkable instances of independent discovery on record, for no fewer than three different investigators, E. S. Fedorov in Russia, A. Schönflies in Germany, and W. Barlow in England, during the years 1890 to 1894 were simultaneously contributing to the complete solution of the problem. They introduced another factor and principle, namely, mirror-image symmetry, repetition as an image seen by reflection from a plane, or "enantiomorphism" (existence in two "enantiomorphous" forms, one the mirror-image of the other) as it is technically termed (see page 131). A large number of additional types of homogeneous structure are at once admitted by the application of this new principle, amounting altogether to 165, thus rendering the total number of possible homogeneous structures, inclusive of the 65 Sohncke point-systems (themselves inclusive of the 14 Bravais space-lattices by specialisation or reduction), no less than 230. Every one of these falls into one or other of the 32 classes of crystals, and thus these classes are completely explained on the simple and obviously correct assumption that a crystal is a homogeneous structure, the points representing the structural units of which are arranged in accordance with some one or other of the 230 geometrically possible types of such homogeneous structures.

This new property of enantiomorphism or mirror-image symmetry is exhibited by the crystalline forms which are not accounted for among



Sohncke's 65 regular point-systems, and both Fedorov and Schönflies established independently and more or less simultaneously that a definition of the symmetrical repetition of parts which includes enantiomorphous similarity as well as identity leads to types which, as just stated, belong to the whole 32 crystal classes.

Pierre Curie, whose name is so familiar to us in connection with the discovery of radium, had previously made it clear that as regards the exterior symmetry of crystals the whole of the 32 classes could only be fully accounted for by admitting as elements of symmetry not only the well-known planes and axes of symmetry, but also a combined plane and axis of alternating symmetry, that is, a new element of symmetry involving a combined rotation about an axis and reflection across a plane, both operations being completed before the second crystal face is arrived at. Curie further deduced two kinds of repetitions, one which left everything exactly as before, and another in which the new units are the mirror-images of the old units, and if he had only followed up the subject from the internal structural point of view, instead of confining himself merely to the external geometrical aspect, he might have anticipated the work of Schönflies, Fedorov, and Barlow, and derived directly from his propositions the whole of the 230 types of homogeneous structures, which the labours of these three investigators have resulted in bringing to light.

The first in point of time to establish the existence of the whole 230 types of homogeneous structures was Fedorov, but unfortunately the three memoirs in which his results are recorded were at first published only in the Russian language, in the *Transactions of the Russian Mineralogical Society* for the years 1885, 1888, and 1890 respectively. Thus it came about that his ideas remained for some years unknown outside Russia. Indeed it was not until he published an abstract<sup>1</sup> in German in 1893, after the publication of the book of Schönflies, *Krystallsysteme und Krystallstruktur*, at Leipzig in 1891, that the work of Fedorov became generally known. The work of Barlow was published later, his chief memoirs being "Über die geometrischen Eigenschaften homogener starrer Structuren und ihre Anwendung auf Krystalle,"<sup>2</sup> and a subsequent memoir<sup>3</sup> published in the year 1897. The methods by which Fedorov, Schönflies, and Barlow arrived at the same goal are interestingly different, and afford an additional testimony to the accuracy of their conclusions, the same exact number of 230 types being the outcome of each. The memoirs are very voluminous, but their essential points may be stated with brevity.

FEDOROV, after developing the known elements of symmetry, the axis, the plane, and the combination of the two, Curie's alternating symmetry, proceeds to show further that two more elements of symmetry are possible, a screw axis and a glide plane. Repetition about a screw axis consists of rotation around and translation along the axis, while repetition about a glide plane consists of reflection across and translation parallel to a plane. He next conceives that crystal structure is space

<sup>1</sup> *Zeitschr. für Kryst.*, 1893, 21, 679.

<sup>2</sup> *Ibid.*, 1894, 23, 1, and 1895, 25, 86.

<sup>3</sup> *Proc. Roy. Dublin Society*, 1897, 8, 527.

partitioned into and filled with parallelohedra, which are equal figures ranged parallel to each other. When plane-faced, they are bounded by parallel pairs of plane faces. Fedorov then shows that the number of plane-faced parallelohedra is restricted to five, the cube, rhombic dodecahedron, elongated dodecahedron, cubo-octahedron, and hexagonal prism, the first being a tri-parallelohedron, the last a tetra-parallelohedron, the second and third hexa-parallelohedra, and the cubo-octahedron a hepta-parallelohedron. They are represented in this ascending order at *a*, *b*, *c*, *d*, *e* in Fig. 448. From these he derives a considerable number of deformed parallelohedra, exhibiting the symmetry of the seven crystal systems, 22 in all, namely, three each for the cubic, tetragonal, and rhombohedral (trigonal) systems, one for the hexagonal, and four each for the orthorhombic, monoclinic, and triclinic systems. When each of these parallelohedra is represented by a point we obtain the 14 Bravais space-lattices, the difference between the numbers 22 and 14 being explained by the fact that certain parallelohedra yield identical space-lattices. It is interesting that the cubo-octahedron, Fedorov's hepta-parallelohedron, that is, a figure composed of seven pairs of parallel faces, is identical with the tetrakaidecahedron of Lord Kelvin, the parallel-faced cell of most general form (a model of which is represented in Fig. 87 on page 146) into which Lord Kelvin showed that space may be partitioned with a minimum superficial area for a given volume, in his Boyle lecture to the Oxford Junior Scientific Club

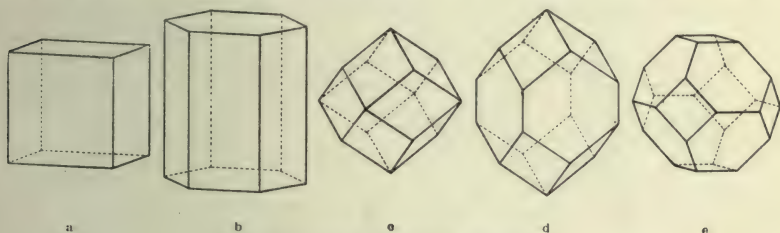


FIG. 448.—Parallelohedra of Fedorov.

in 1893, following up and collecting together the results of several of his previous memoirs, particularly one on the "Homogeneous Division of Space,"<sup>1</sup> and an earlier one "On the Division of Space with Minimum Partitional Area."<sup>2</sup>

Fedorov thus appears to have three distinct things in view, namely, the partitioning of space by similar parallelohedra, the close fitting of these bodies so as entirely to fill the space thus partitioned, and the homogeneous assemblages of points produced by considering each parallelohedron as represented by a point, such points being chosen analogously from all the similar parallelohedra. So far, we have seen, this latter aspect of his theory of crystal structure brings us merely to the Bravais space-lattices.

He now goes further, by assuming that his parallelohedra may be made up of a number of identically similar polyhedra, which he calls "stereohedra," and these may be differently orientated. The analogous points representing these stereohedra constitute a regular point-system, the points of which may obviously be grouped into clusters the mutual arrangement of which is that of a space-lattice, for the parallelohedra corresponding to the clusters form by their representative points a space-lattice, as we have just seen. Employing the method of coincidence movements, the stereohedra and their representative points first arrived at by Fedorov corresponded to the 65 regular point-systems of Sohncke, and so far there was no real advance, beyond the fact that an interesting theory of crystal structure had been put forward, which agreed with Sohncke's truly valid conclusions and gave us at the same time a physical interpretation of them in the division of the crystal into corresponding cells, a

<sup>1</sup> *Proc. Roy. Soc.*, 1894, 55, 1.

<sup>2</sup> *Phil. Mag.*, 1887, 24, 503.



reversion more or less to Haüy's conception of the structural units having a definite shape.

But Fedorov went further in deriving also those stereohedra and their representative points which are the mirror-images of each other, and each corresponding enantiomorphous pair of these he called a "double system." Indeed he distinguishes altogether three kinds of space-partitioning cells and their representative points, namely, (1) symmorphous systems, the elementary figures or cells of which have the same symmetry as the system itself; (2) hemisymorphous systems, consisting of two analogous simple systems, which together make up a double system, the latter not being symmorphous; and (3) asymmorphous systems, in which adjacent figures are differently orientated. After investigating every kind of homogeneous structure possible on these assumptions, both of cells and of points representing them, he came to the conclusion that there were 230 such systems.

These systems 2 and 3 doubtless cover the cases of those polymolecular structural units in which the constituent molecules are not arranged parallelwise. Indeed, the stereohedra may be such chemical molecules, or they may even be parts of molecules, especially in the cases of complicated molecules and double salts such as the monoclinic series  $R_2M\left(\overset{S}{\text{Se}}\text{O}_4\right)_2 \cdot 6\text{H}_2\text{O}$ .

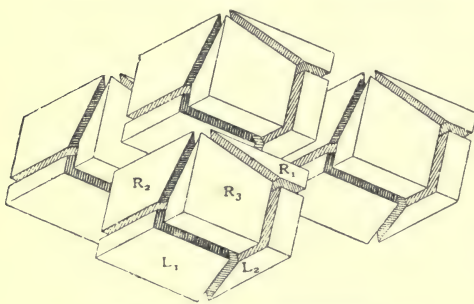


FIG. 449.—Fedorov's Stereohedra.

Fig. 449 will render clear this idea of stereohedra. It represents a rhombohedral system of stereohedra of two kinds, R and L, one being the mirror-image of the other; 6 stereohedra, 3 of each kind, go to form each rhombohedral combined-system. A series of points, similarly situated one within each stereohedron R, would constitute a Sohncke point-system, while a double-system is obtained by adding a similar L series. If a single point be taken to represent analogously each rhombohedral set of 6 stereohedra, a rhombohedral space-lattice is produced.

SCHÖNFLIES treated the subject from another standpoint. He began by defining regularity of structure on Wiener's lines by saying that every molecule of an assemblage has the remaining molecules arranged collectively about it in a manner which may be either that of identity or of mirror-image resemblance. As only such of Jordan's groups of movements are concerned in crystal structure as are capable of producing a space-lattice, Schönflies only applies mirror-image operations to such groups. In doing so he employs not only the ordinary planes and axes of symmetry and the screw axes of Sohncke, but also gliding planes of symmetry, which involve reflection over a plane combined with translation parallel to the plane, and the planes of alternating symmetry of Curie. He further proves that in the possible groups of space-operations the only symmetry axes are those characteristic of space-lattices, namely, digonal, trigonal, tetragonal, and hexagonal axes. Carrying out, therefore, all the possible space-operations which conform with these premises, and which lead not only to the 65 Sohncke point-systems but also to point-systems involving mirror-image repetition, and which, moreover, involve also two opposite kinds of screw motions, Schönflies arrived at the same final goal as Fedorov, namely, that there are 230 groups of such space-operations possible, corresponding to 230 homogeneous structures possible to crystals. Their distribution among the 32 classes of crystals will be found given in the table at the end of Chapter XXXI.



Just as Fedorov connected his main result—the discovery of these 230 types of homogeneous structures which fall into and account for the whole 32 classes of crystals—with a hypothesis of his own regarding crystal structure itself, so also Schönflies regarded his similar main result as a stepping-stone to a molecular theory of crystallised matter. He, too, imagines each representative point as placed within a cell, an elementary cell or “Fundamentalebereich” as he calls it, within which lies the molecule, which does not necessarily fill the cell with its chemical matter; moreover, the form of the cell itself is in general indeterminate, but subject to certain conditions which indicate a polyhedral character. In general, also, there will be two kinds of such polyhedral cells, which are mirror-images of each other. Schönflies is thus obviously attempting to ascertain what conditions of shape and character of the chemical molecule are the basis of the constitution of crystals, and although it is not necessary to follow him in his hypothetical work in this direction, the fame of Schönflies is assured as having, in a manner altogether different from that of Fedorov, discovered and defined the 230 types of homogeneous structures which alone are possible to crystals, whether the units be considered as cells or as points. If we accept the work of both Fedorov and Schönflies as certainly valid when points are taken to represent the crystal units, whatever they are, we have accepted a solid fact, which forms the basis of the true and complete theory of crystal structure.

BARLOW arrived at the same conclusion, that there are 230 kinds of homogeneous structures which belong to the 32 classes of crystal symmetry, from yet a third aspect. He takes his stand on a precise definition of a homogeneous structure, which he gives in the following words, which will be found in a summary of his work<sup>1</sup> given to the Mineralogical Society on November 19, 1895: “A homogeneous structure is one every point within which, if we regard the structure as without boundaries, has corresponding to it an infinitude of other points whose situations in the structure are precisely similar, so that all of the infinite number of geometrical point-systems respectively obtained by taking all similarly situated points are regular infinite point-systems, defined by Sohncke as systems of points such that the arrangement about any one of these points of the rest of the points of the system is the same as it is about any other of them.” So far, then, Barlow follows the ideas of both Wiener and Sohncke, but defines the homogeneous structure in more precise terms, and does not encumber it with any further postulate about the corresponding partitioning of space into cells.

The essence of Barlow's work is thus its generality, neither points nor molecules, nor anything in particular, being its foundation, but merely the geometric conception of the arrangement of identically similar parts in a homogeneous rigid structure of any kind whatsoever. Indeed in his paper to the Mineralogical Society (*loc. cit.*) he goes so far in getting rid of the idea of shape of the units as to represent them by plaster models of the human hand, and numerous possible symmetrical arrangements of right and left hands are figured in the plates accompanying his paper. In another memoir he employs a pile of cannon balls as an example of a homogeneous structure, and in yet another he uses a stack of cubes. Perhaps the latter is most instructive of all, as to the nature of his method. He directs attention to a corner of any one of these cubes, and to the fact that it is a point in which eight different cubes of the stack touch each other. Next he indicates some particular point within the cube, which may be selected anywhere, but most instructively near the corner in question. He then shows that there are two other points equidistant from the same corner from each of which the appearance of the whole structure is the same as from that first point; also that there are three other similar points near each of the other seven corners of the cube, from which the outlook is precisely the same. There are thus 24 points within this selected cube from which the stack of cubes would look exactly the same to the eye of a fly, for instance, situated at each of these points in succession,

<sup>1</sup> *Mineralogical Magazine*, 1895, 11, 119.

assuming that the whole structure were transparent and non-refractive. The 24 points thus located form a 24-point group of Sohncke (No. 60, the octahedral 24-point system, Fig. 520, page 618).

But Barlow goes a stage further, for he shows that there are three other points near each corner of the cube, from each of which the appearance of the stack is the same as before, except that everything is now inverted, just as if its reflection were being observed in a mirror. These points together make up a second Sohncke 24-point group. He regards identity with its own image as the only property of homogeneity which can raise the symmetry of a homogeneous structure. Starting, therefore, in this manner with the 65 Sohncke point-systems, which his method likewise first arrives at, he inquires which are capable of possessing the additional property of identity with their own images, and how many arrangements there are in which this may be so, and finally arrives at the 230 possible varieties of homogeneous structures.

The above example afforded by a stack of cubes is a very simple case, but it is easy to introduce the sort of complication which many crystals show by imagining each cube to have subsidiary points similarly distributed about it in two ways, firstly so that the appearance of the whole structure from any one of the second 24 points above referred to is the same as from one of the first set of 24 points, and secondly so that the appearance is not the same. In both cases the structure is obviously a homogeneous one, points in each cube being taken analogously, but the former structure has the full cubic symmetry, being identical with its own image, while the latter has not, but corresponds to a so-called hemihedral class of the cubic system, the pentagonal-icositetrahedral class of which cuprite, the lower oxide of copper,  $\text{Cu}_2\text{O}$ , is a characteristic naturally occurring example.

Barlow gives many reasons for regarding as untenable the arguments of Fedorov in support of his attempt to determine the shape of the ultimate structural units of crystals, and deprecates all reference to the nature of the crystal faces in connection, at any rate, with the investigation of the nature of homogeneous structures. More recently Barlow himself, however, has advanced, in collaboration with Sir William Pope, a theory of space-packing as he assumes it to occur in crystals, that of the closest packing of spheres, the sizes of which are proportional to the chemical valency of the atoms the spheres of influence of which they are supposed to be. This "theory of valency volumes," however, will later be shown to be erroneous. But in his arguments concerning homogeneous structure he most wisely avoids all speculative theories, and confines himself to the strict geometrical problem in hand. He says, "We have to ask ourselves what significance Fedorov attaches to his partitioning of a crystal structure? Is it suggested that when a crystal dissolves, its parts will under any circumstances retain shapes which, if fitted together, fill space, or, to put it more precisely, that the solid angles and edges of the cells are none of them vacuous or structureless in the unbroken structure, but always occupied by matter which, when the structure breaks up, can retain its situation relatively to other matter belonging to the same cell? Such a proposition is so unlikely that to state it is almost to refute it. But if the partitioning into cells of a definite outline capable of filling space is, in the case of crystals, a mere geometrical fiction, what stress can be laid on the relative inclinations of the plane faces of the cells, and what significance is there in the cell walls having plane faces at all. Instead of dwelling on differences between the various kinds of plane-faced cells,—an investigation which may or may not ultimately prove to be of any importance,—we ought to strive after some altogether broader treatment of the subject, which will classify the various kinds of partitioning possible in a perfectly general manner, without absolutely rejecting any. The fact that bodies which form crystals are capable of passing to a liquid state and back again to the crystallised condition without breaking up into their constituents, and the evidence we often have of the survival in the liquid of some portion of the symmetry of arrangement of parts previously in the solid, notably in the cases of those bodies which rotate the plane of



polarisation, lead us to conclude that crystallised matter can be broken up into particles or units which are all alike, and each of which has parts or properties that have some definite arrangement relatively to one another. In some cases there is evidence of the survival in the dissolved crystal of two kinds of arrangement, which are enantiomorphous, *e.g.* racemic compounds can mechanically or otherwise be shown to be composed of two isomers which are respectively right-handed and left-handed but otherwise alike."

To the evidence adduced as above by Barlow of the survival in the liquid substance of some portion of the crystalline properties, such as the capability of rotation of the plane of polarisation and the exhibition of enantiomorphism, may now be added that offered by the viscous and more mobile oily substances which have been shown by Lehmann to exhibit uniaxial double-refraction and to act as so-called "liquid crystals." It has also been abundantly proved, from the author's own researches, that the elementary atoms in the chemical molecule do reveal themselves in the crystal as occupying distinct and definite positions in the molecule, and it is highly probable that the class of crystal symmetry which a substance displays is due to this specific orientation of the atoms, together with the mutual arrangement of the individual molecules in the cases of polymolecular units, while the system to which the crystal belongs is the function of the space-lattice formed by the arrangement of the whole molecules (or polymolecular-group structural units) or their representative points.

On the general lines now thus indicated Barlow proceeded to investigate all the possible kinds of homogeneous structures, as already stated. In doing so it may be useful to say that he took into account (1) the different sets of axes of rotation present, (2) the centres of symmetry (a centre of symmetry being equivalent to Curie's rotation about an axis combined with reflection across a plane), (3) the planes of symmetry which have the enantiomorphously related points directly opposite on their two sides, (4) the symmetrically placed planes with accompanying centres, such as those of the two types of structure identical with their own mirror-images, which have no centre or planes of symmetry, and (5) the points and lines of intersection of these various elements of symmetry. He pointed out that in general the regular point-system of Sohncke represents a class of homogeneous structure which is not identical with its own mirror-image. Further, that the additional property of identity with mirror-image can be displayed by homogeneous structures in three different ways, leading to still other types of symmetry, either (1) across a centre of symmetry so that they are oppositely orientated in every direction, or (2) across a plane or planes of either ordinary or gliding symmetry, or (3) they are opposite each other with reference to one direction and are at the same time orientated at right angles to each other, this method of repetition having an axis of alternating symmetry, as used by Curie. Barlow only requires this last mode of repetition to explain the 2 classes (types) of tetartohedral symmetry of the tetragonal system (crystal-class 10), the other 228 classes (types) being derived by the methods already previously quoted.

Barlow's method of deriving the additional 165 types of homogeneous structures, beyond the 65 Sohncke point-systems, possesses the advantage of distinguishing clearly the enantiomorphous types from those possessing mirror-image symmetry, and of showing the mutual relations of the two enantiomorphous types of which a double system consists; and it also indicates the exact positions of the centres and planes of symmetry. The points which lie at these centres or on axes or planes of symmetry Barlow calls "singular points," and these are very few in number compared to the other points. For instance, when a point occupies the centre of each cube in the stack of cubes referred to on page 569, there are two sets of 24 points, and thus 48 in all, surrounding each such central or "singular" point.

The extraordinary agreement between these three independent investigators, Fedorov, Schönflies, and Barlow, renders it practically certain



that the problem of the homogeneous partitioning of space, as it is possible in crystals, has now thus received a complete solution. With the establishment of the 230 types of homogeneous structures, each compatible with and referable to one of the 32 classes of crystals, the geometrical theory of crystal structure has attained what in all probability will prove to be finality. It must be quite understood, however, that the purely geometrical problem only is referred to. The moment we begin to invest the space-units or cells with definite shapes, such as the parallelohedra of Fedorov and of Lord Kelvin, the "Fundamentalebereiche" of Schönflies, or even the spheres of influence of Barlow, we simultaneously introduce controversial questions. Standing quite clear of these, and representing the structural units of the crystals by points or nodes, we are on absolutely sure geometrical ground. Whatever may be the parts of which a crystal consists, they must be arranged according to one or other of the 230 possible arrangements of such points as types of homogeneous structures, of which Sohncke systems and Bravais space-lattices are special cases. Moreover, as Barlow suggests, the material occupying the *Fundamentalebereiche* of Schönflies, or represented by a generalised point-system, may always be supposed to be grouped about the nodes of the underlying space-lattice if required, so that what were at first regarded as independent units (the ultimate units, the chemical atoms) come to be considered as the parts of a composite or grosser structural unit (the chemical molecule or small group of molecules), which is represented as a whole by a nodal (or any) point of the space-lattice.

Now Lord Kelvin, in his Boyle lecture at Oxford in 1893, laid special emphasis on the importance of the Bravais space-lattice, and there can be no doubt that his far-seeing and prescient judgment in this matter is entitled to great weight. Indeed the whole of the remarkable investigations which have now been detailed emphasise this point, whether it were the intention of the authors to do so or not. The space-lattice it undoubtedly is which determines both the crystal system and the compliance with the law of rational indices.

After the completion of the work of Fedorov, Schönflies, and Barlow, and mainly owing to a study of the results of Schönflies, with which alone he was at first acquainted, Sohncke further developed his theory of crystal structure in two important communications.<sup>1</sup> This more generalised form embodies many of the results of Fedorov, Schönflies, and Barlow, and if modified in a manner suggested by Barlow, by stipulating that the component point-systems which Sohncke refers to shall have all their coincidence-movements in common, it covers the cases of all but one or two of the crystal classes. In this more generally acceptable form it has been recommended by von Groth, in his Address to the British Association at Cambridge in 1904. As quoted by him it is expressed as follows :

**A crystal—considered as indefinitely extended—consists of  $n$  interpenetrating regular point-systems, each of which is formed from similar atoms ; each of these point-systems is built up from  $n$  interpenetrating**

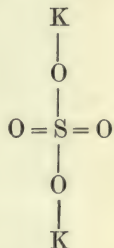
<sup>1</sup> *Zeitschr. für Kryst.*, 1888, 14, 435, and 1892, 20, 445.

space-lattices, each of the latter being formed from similar atoms occupying parallel positions. All the space-lattices of the combined system are geometrically identical or are characterised by the same elementary parallelepipedon.

We may add to this statement the following corollary :

The combined system conforms to some particular one of the 230 possible homogeneous arrangements in space, and determines which one of the 32 classes of crystal symmetry shall be exhibited in the exterior form of the crystal ; the space-lattice determines the crystal system, and the interfacial angles, and brings about the fulfilment of the law of rational indices.

According to this statement we should expect, for instance, in the case of our typical crystal of potassium sulphate, the chemical formula of which may be graphically expressed as in the margin, that the structure consisted of three regular point-systems, the first being of sulphur atoms, the second of four times as many oxygen atoms, and the third of twice as many potassium atoms as there are sulphur atoms ; the three systems would probably interpenetrate in such a manner as to produce equilibrium, being so arranged that the sulphur-atom system lies centrally with



respect to the other two, and the potassium-atom system in such wise as would affect chiefly the vertical direction. For this orientation corresponds to the directional changes which occur when the sulphur is replaced by selenium, and when the potassium is replaced by rubidium or caesium. The arrangement of each cluster of seven atoms corresponding to the molecule  $\text{K}_2\text{SO}_4$  would thus correspond to what we have learned to call the stereometric arrangement of the atoms. Each of these seven atoms composing the molecule would give rise to a space-lattice (composed of itself and its analogous points of adjacent molecules) and all these seven interpenetrating space-lattices would be geometrically identical, the atom being the unit of the space-lattice, although it may be considered equally well as the representative point of the whole molecule. The combined system of the seven, however, corresponding to the cluster of atoms in the whole molecule, would determine that the symmetry should be that of the holohedral class, rather than that of any other class, of the orthorhombic system ; while the space-lattice formed by each or any one of the seven atoms, analogously chosen from all the clusters of seven throughout the whole assemblage (and which chosen atom indeed may be taken as a point representing the molecule equally as well as does the centre of gravity of the molecule), determines that the system is the orthorhombic one, and fixes the interfacial angles and the crystal elements. The matter is not quite so simple as this, however, as the alkali sulphates have four chemical molecules to the grosser structural unit, and the exact arrangement will be described in Chapter XXXIII., when discussing the results of the X-ray analysis of these salts.

One of the chief results of the author's comparative work on the alkali sulphates and double sulphates and the analogous selenates has



been to prove beyond all shadow of doubt that the atoms and their enveloping spheres of influence do occupy distinct and characteristically orientated portions of space within the crystal structure. Two opposing forces acting between such atomic centres are alone necessary for the stability of the structure, a repulsive force dependent on the kinetic energy of the atoms, and an attractive force of the combined nature of gravity and chemical affinity, in accordance with the well-known selective character of chemical combination.

This modified Sohncke method has the great merit of simplicity, and of emphasising the undoubted importance of the space-lattice. It is equivalent to the assumption that two or more regular point-systems, consisting of different kinds of atoms (that is, of different chemical elements), may be interlaced, interpenetrating in such a manner as to produce equilibrium, the condition for which is that the different point-systems shall be built up of space-lattices of identical dimensions. Moreover, it agrees perfectly with the experimental facts indicating definite orientations for the different atoms in the molecules. It is undoubtedly legitimate to consider each or any atom in the chemical molecule as representative of the molecule, quite as much so indeed as to take the centre of gravity as the representative point. Also it must be clear that the interlaced point-systems, and therefore also the interpenetrating space-lattices composing them and equal in number to the number of atoms in the molecule or polymolecular group, will together form one of the 230 possible types of homogeneous structure.

This later development of his theory by Sohncke agrees for the great majority of cases with the conclusions of Fedorov, Schönflies, and Barlow. But Sohncke has considered the division of the molecules, in the few outstanding cases which his theory does not explain, into two enantiomorphous sets very improbable. The overwhelming number of cases where all agree, as just mentioned, are those in which, on Sohncke's theory, the molecules are all congruent, and Sohncke considered congruency of the molecules to be an essential condition of crystal structure. But the few remaining cases are so completely explained by the assumption of the three other investigators that two enantiomorphous sets of molecules are simultaneously present in the crystal—as there are, for instance, when there is “external compensation” between the two opposite kinds of molecules in a racemic compound<sup>1</sup>—that there would appear to be more ground for accepting their assumption as correct, especially as it is geometrically possible, than for rejecting it, and no other explanation would appear to be geometrically valid.

A very able mathematical review of the whole subject has been made by H. Hilton in his *Mathematical Crystallography*.<sup>2</sup> On this particular point, where the opinion of a mathematician is of special importance, experimental evidence only just beginning to be available by the use of the new X-ray diffraction method, Hilton says :

<sup>1</sup> A compound of similar nature to racemic acid, which is the optically inactive molecular compound of dextro (right-handedly optically active) and lævo (left-handedly rotating) tartaric acids.

<sup>2</sup> Oxford, 1903, p. 251.



"The individual molecules have no symmetry in general" (which the author takes to mean that Hilton agrees that the stereometric arrangement of the atoms in the molecule, while definite, is not necessarily symmetrical); "they are all congruent if the space-group has no operation of the second sort" (such as that involving reflection over a plane); "if, however, it has such an operation the molecules may be divided into two sets, such that the molecules of either set are congruent to all the molecules of the same set and enantiomorphous to those of the other. Some authors have objected to this division of the molecules of a crystal into two enantiomorphous sets as improbable. It is, in fact, in most cases possible to avoid having recourse to this division, . . . but the weakness of the" (alternative) "method" (of grouping into congruent molecules) "lies in the fact that it cannot be used to explain the structure of crystals of every class, without supposing that these congruent molecules may interlace with one another, an idea which hardly commends itself to a physicist." But Hilton concludes his analysis by adding: "The series of points representing the constituent parts of a crystalline solid are the points of a series of similar and similarly orientated lattices, any one of which represents the translations of the group. We may therefore apply without appreciable modification Bravais' explanation of cleavage, the occurrence of crystal faces, and the law of rational indices."

These views of Hilton will be observed to be in full agreement with

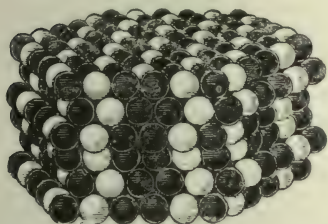


FIG. 450.—Barlow's conception for Right-handed Quartz.

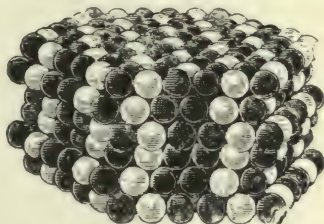


FIG. 451.—Barlow's conception for Left-handed Quartz.

those already expressed in previous pages by the author. He also gives an excellent account of the derivation of the 230 types, following the method of Schönflies with a somewhat different nomenclature.

Previous to the discovery of the X-ray method, several attempts had been made to allocate specific types of homogeneous structure to particular crystallised substances. Thus the two enantiomorphous forms of quartz, right-handed and left-handed, have been referred by Sohncke to two of his types which are similar, except that one has a right-handed screw and the other a left-handed screw coincidence-movement, namely, Nos. 18 and 19 (Fig. 491, page 609), the right and left compound three-point-screw systems. Barlow has likewise published a similar conception of the two varieties of quartz, illustrated by the two models constructed of india-rubber balls reproduced in Figs. 450 and 451, the white spheres representing silicon atoms and the black ones (twice as many) oxygen atoms, corresponding to the composition  $\text{SiO}_2$ . The helical character is clearly displayed by the white balls, which are obviously arranged in a right-handed screw in Fig. 450 and in a left-handed helix in Fig. 451. The author has also shown that the isomorphous group of sulphates and selenates of the alkalis, of which potassium sulphate,  $\text{K}_2\text{SO}_4$ , is the first member, are

referable to a particular one of Barlow's types, which, while really of rhombic symmetry, is of pseudo-hexagonal (slightly deformed hexagonal) type, in accordance with the pronounced pseudo-hexagonal nature of the crystals. It is only in cases where the optical properties of a substance have been exhaustively worked out, however, as in the cases of quartz and of the potassium sulphate group of salts, that such attempts are likely to meet with success. For generally there are several isomorphous types possible among the 230, and only a large amount of experimental data can enable us to decide between them. It will be shown, however, in Chapter XXXIII. that the structure of a considerable number of substances has now been very satisfactorily unravelled by means of the new X-ray spectrometric method.

Having thus now dealt with the whole of the original investigations into the nature of homogeneous crystal structure, we may leave the subject in general agreement with the view of von Groth, who has had unique means of becoming acquainted with the whole of the details of the published memoirs of all the workers concerned, in his capacity of editor of the *Zeitschrift für Kristallographie*; that is, we may accept the Sohnckian theory of regular point-systems, in the latest form given to it by Sohncke and as perfected by Fedorov, Schönflies, and Barlow, as affording a fully satisfactory explanation of crystal structure, by providing us with 230 distinct types of homogeneous structures, the total possible, and which among them account for all the 32 symmetry classes of actual crystals. Sohncke is undoubtedly correct as far as he is in agreement with Fedorov, Schönflies, and Barlow, and for the rest, where Sohncke's method is insufficient, the agreement of these three latter observers among themselves is a guarantee that their purely geometrical work also bears the stamp of accuracy. On the border line, we have the choice of either the method of Sohncke or of that of the three other investigators, for those cases of assemblages in which the possibility of the coexistence of two enantiomorphous sets of molecules is involved; and if we accept the suggestions of Barlow for the modification of the method of Sohncke, all are practically brought into line.

If the crystal be that of a chemical element, there is obviously only one kind of atom and one regular point-system; but when the crystal is that of a chemical compound the arrangement of the combined system corresponds with the equilibrium of the forces with which similar and dissimilar atoms act on each other, that is, on the stereometric arrangement of the atoms within the molecule. We must include in such equilibrium any mechanical or other physical forces which may likewise be operative in the production of the solid crystal, in the laying of the molecules in position, and possibly in the arrangement of two, three, or four molecules to form the group acting as the unit of the space-lattice. On fusion, solution, or evaporation of the crystal the system breaks up into separate freely moving molecules, when they lose their parallel or enantiomorphous arrangement which they had assumed with respect to each other in the crystal.

The following may prove to be a useful summarised statement of the



geometrical theory of crystal structure which has now been discussed in the foregoing pages :

The 14 space-lattices of Bravais are the foundation of crystal structure. Sohncke's 65 point-systems express the number of ways in which identical repetition can occur, the points being symmetrically and identically arranged about axes of symmetry, sometimes spirally about screw axes. The points may be grouped in sets the centres of gravity of which form a Bravais space-lattice, so that a Sohnckian system consists in general of 2 or more interpenetrating space-lattices. Schönflies, Fedorov, and Barlow introduced the further principle of enantiomorphous similarity ; for to each Sohnckian system not identical with its own mirror-image there corresponds another, enantiomorphously symmetrical with it, and the introduction of the principle together with the various modes of combining the two forms, including interpenetration, afford the additional 165 systems, thus making a total of 230 types each having its own distinct system of coincidence operations.

Hence we come to the final conclusion that the skeletal framework of crystal structure is the molecular or polymolecular space-lattice, each point representing a molecule or small group of molecules ; and that the detailed ultimate structure is the atomic point-system. The latter determines the class of symmetry (which of the thirty-two classes is exhibited), and therefore governs any hemihedrism or tetartohedrism, as the development of less than full systematic symmetry used to be called. But it is the space-lattice which governs the crystal system, that is, which determines whether the symmetry be cubic, tetragonal, rhombic, monoclinic, triclinic, trigonal, or hexagonal, and which also determines the crystal angles and the disposition of faces in accordance with the law of rational indices, the law which limits the number of possible faces to those which cut off small whole-number relative lengths from the crystal axes. Indeed, it is because only those planes which contain the points of the space-lattice are possible as crystal faces that the law of rational indices obtains. For any three points of the space-lattice determine a plane in which similar points are analogously regularly repeated, and which is a possible crystal face obeying the law of rational indices. Moreover, those facial planes which are most densely strewn with points are of the greatest crystallographic importance, being what are known as the primary faces, either parallel to the crystal axes or cutting off unit lengths therefrom, as well as being usually the planes of cleavage.

As the space-lattice units are all sameways orientated, any one atom of the molecular or polymolecular grosser unit might be equally well chosen as the representative point of the lattice, so long as a similar choice were made in every space-lattice unit, and the resulting space-lattice would be the same whichever atom were so selected. Consequently, the space-lattice is afforded by the similarly (identically) situated atoms of the same chemical element throughout the crystal structure. The combined point-system (one of the 230 possible point-systems) may thus be considered to be built up of as many identical but interpenetrating space-lattices as there are atoms in the space-lattice grosser unit.



It has been considered essential to deal at some length with this most important modern advance in our ideas of crystal structure, inasmuch as all future work both in chemistry and in the physics of solids will have to take account of it, and all practical crystallographic investigations must, to be of value, be carried out with these facts borne in mind. For it is only by organised experimental effort, directed to the study of definitely chemically related substances, that an adequate number of facts of indisputable authority can be marshalled to enable us to carry our present knowledge further to its logical conclusion, when we shall be enabled to predict the crystalline form from the given chemical constitution. So far as the geometrical theory has been taken in the preceding pages, it is in full accordance with experimental facts as well as with mathematical geometry, the one confirming the other to a degree which ensures that the truth has so far been arrived at. Moreover, it is confirmed in a most remarkable and conclusive manner by the X-ray analysis of crystals now so rapidly developing, an account of which will be given in Chapter XXXIII.

## CHAPTER XXXI

DENSITY, VOLUME, AND STRUCTURE—THE 14 SPACE-LATTICES—MOLECULAR DISTANCE RATIOS—THE 65 REGULAR POINT-SYSTEMS AND THE 230 SPACE-GROUPS

**Density and Structure.**—The relative density of crystals—which is afforded by the experimental determination of their specific gravity as compared with that of water at 4° C., the temperature of its maximum density—has acquired a far greater importance than formerly, owing to the fact that in any series of isomorphous substances of known molecular weight it enables us to calculate the relative volumes of the molecular or polymolecular unit cells of the structural space-lattices of the various members of the series. Even if the crystal-unit be not the simple chemical molecule, but is polymolecular, the information is equally valid; for the type of symmetry is the same for all the members of an isomorphous series, and the number of chemical molecules forming the crystal-unit will be the same for each. Also further, by combining this knowledge of the molecular volumes with that of the crystallographic axial ratios already gained from the goniometrical investigation of the substances, we are able to calculate the relative dimensions of the space-lattice cells, that is, the distances apart of the centres of gravity or other analogous points of the chemical molecules or polymolecular groups in the three (or four) directions of the crystallographic axes, these relative distances being termed the “**molecular distance ratios**” or “**topic axial ratios**.” For it was shown in the preceding chapter (XXX.) that the structure of a crystal is a homogeneous one, which can be represented as regards the grosser structure by a system of points, each point standing for a chemical molecule or small group of molecules (crystal-unit), or for any one of the atoms composing the molecule or group and representing it; these points, if joined by straight lines, form a space-lattice, one of the 14 possible space-lattices of Bravais. The later form of Sohncke’s theory of crystal structure, as harmonised with the work of Schönflies, Fedorov, and Barlow detailed in Chapter XXX., is now generally accepted, as being in accordance with all the experimental facts concerning crystals acquired up to the present, as well as with the completion of our geometrical knowledge of the possible types, now known to be 230 in number, of homogeneous structures. In its essence it assumes that the crystal

is built up of as many similar interpenetrating point-systems (space-lattices) as there are atoms in the chemical molecule or polymolecular crystal-unit, the relations of any one such point-system with respect to any other being consequently expressed by and corresponding to the relative (stereometric) positions of the atoms with respect to each other in the molecule or group; such relative positions determine to which of the 230 types the combined point-system conforms, and therefore also the particular class (out of the 32 possible classes of symmetry) to which the crystal conforms; while the character of any one of the space-lattice point-systems (all being similar) determines which system of symmetry among the seven possible systems the crystal shall exhibit. That is to say, the space-lattice is only sufficient to determine the system, but not the class; for all space-lattices are essentially holohedral. To determine the class is the function of the combined, detailed, point-system.

Suppose we consider our typical crystal of potassium sulphate once more,  $K_2SO_4$ , a substance exceptionally rich in regard to the lessons which may be derived from it. A molecule of this crystalline salt consists of seven atoms, two of potassium, one of sulphur, and four of oxygen. The grosser unit (crystal-unit) of the structure is shown by X-ray analysis (as described in Chapter XXXIII.) to consist of a group of four chemical molecules, *i.e.*  $4K_2SO_4$ . The system in which the salt crystallises has been experimentally shown in Chapters IV. and VIII. to be the orthorhombic. This fact is determined by the arrangement of the space-lattice, formed by the point-system in which the points are analogous points, one taken from each group of four chemical molecules present (as indicated by the X-ray analysis). Equally as well as if we took the centre of gravity of the four-molecule group, we can take any atom within any of the 4 molecules as the analogous point. We can, in fact, take all seven atoms of each molecule in turn, or indeed all seven simultaneously. Considering a single molecule for the sake of simplicity, we can readily imagine seven exactly similar models of the space-lattice constructed, say of marbles or indiarubber balls, to represent points, and if we stretch the imagination sufficiently far as to assume the structures to be held together by suitable forces and not by means of solid links, we can suppose the seven to be interpenetrable and to be made almost to coincide. We can then push these seven models one within the other till they are nearly identical, so as to bring every seven points, one similarly situated point from each model in each case, into close proximity, closer than the points of any one and the same model, and also so that the seven points thus congregated together about every point (representative of the cluster) of the common space-lattice are arranged or spaced as are the actual atoms or their spheres of influence in every molecule of the substance; thus, instead of a single point representing a molecule, seven points so represent it, and these seven are arranged among themselves stereometrically, as described on page 573 in Chapter XXX. As there are four molecules to the space-lattice crystal-unit, we have also to consider the mutual arrangement of the four chemical molecules in each group. This, however, will be left to the chapter in which the X-ray analysis of the alkali sulphates is



discussed (Chapter XXXIII.). In the case of potassium sulphate the single sulphur atom will be innermost and the two potassium atoms situated about it symmetrically in such wise as affects chiefly the vertical axis of the crystal, in accordance with the experimental facts revealed by the investigation of the changes produced by replacing the atoms of one metal by those of another metal of the same alkali family group. We thus gain a very fair idea of the structure of a typical crystal of potassium sulphate, and of the nature of crystal structure in general, and our idea will be rendered still clearer when we come to the description of the details of the atomic distribution as revealed by the X-ray analysis. For it has been conclusively shown by the whole of the author's investigations of isomorphous salts, that the atoms or their spheres of influence do take up specific orientations within the molecule, and this result is absolutely and beautifully confirmed by the wonderful X-ray revelations.

**Molecular Volume.**—Now, as the elementary parallelepipeda of the space-lattice will obviously correspond to the molecular or polymolecular cells of which the crystal substance is built up, it follows that the "molecular volume," obtained by dividing the molecular weight of the chemical compound by the specific gravity of its crystals, means in these cases of isomorphous substances, the structures of which are certainly of the same type, the relative volume of the elementary parallelepipedon of the point-system or space-lattice which represents that type; for the points are, as we have seen, strictly analogous ones within the molecules or molecular groups, one in each, representative of the molecule or group. The fact of the crystal-unit being polymolecular, as already stated, need not even be considered; for the number of chemical molecules composing the crystal-unit, the grosser structural unit, is certainly the same for all the members of an isomorphous series. It has to be remembered that the constant "molecular volume" is not an absolute but a relative one, strictly comparable, however, so long as the type of structure is analogously similar, as it is for all the members of an isomorphous series. We can divide out in common, therefore, by the number of molecules in the crystal-unit, when the latter is polymolecular, without altering in the slightest the relative volumes expressed by the "molecular volumes," indeed we are only giving "molecular volume" its simplest expression.

The quotient  $\frac{\text{molecular weight}}{\text{specific gravity}}$  thus acquires from the above considerations a vastly greater importance, and when it is remembered that in the crystallographic axial ratios  $a : b : c$  we have the directional relative dimensions of the elementary parallelepipedon of the crystal structure, expressed in terms of  $b = 1$ , it will be clear that not only are the relative volumes of the parallelepipeda of different members of the series actually afforded by the corresponding values of this quotient, the so-called "molecular volume," but that if we combine the latter with the crystallographic axial ratios we obtain a relative measure of the dimensions of the molecular or polymolecular cell in the three (or four if hexagonal) directions of the crystal axes, for the several members of the series.

The meaning attached to the term molecular volume has in the past

been a somewhat erroneous one, for it is certain that a comparison of the quotient  $\frac{\text{mol. wt.}}{\text{spec. gr.}}$  for two solid substances of entirely different chemical constitution does not afford us necessarily any information of real value. For the type of crystal structure may be, and in general is, quite different. The number of chemical molecules to the crystal-unit (which is the space-lattice unit) will not necessarily or even usually be the same. But in the case of a series of the most strictly isomorphous ("eutropic") compounds we are certain that the structure is analogous and absolutely comparable, only differing slightly in cell dimensions as one chemical element of the family group constituting the series is replaced by another, in accordance with the law revealed by the work on the sulphates and selenates that the structural dimensions are functions of the atomic weights or atomic numbers of the interchangeable elements. Hence, in these cases we are on sure ground, and the comparison of the molecular volumes and of the corresponding directional dimensions of the molecular or polymolecular cells of the space-lattices is most instructive.

**The Fourteen Types of Space-lattice.**—Before passing to the discussion of the mode of combining the molecular volume with the crystallographic axial ratios, in order to arrive at these directional dimensions of the space-lattice cells, it is essential that the nature of the fourteen space-lattices, the elementary parallelepipeda of which represent the molecular or polymolecular cells, should be thoroughly understood. They may be divided into seven groups, corresponding to the seven crystal systems, which may be conveniently considered in descending order of symmetry.

The following five facts are fundamental concerning these 14 Bravais space-lattices, considering their nodes as points and therefore as being without shape :

- (1) They all possess the **homogeneity** characteristic of crystals.
- (2) They have representatives among them of **all** the seven crystal systems, and indeed the type of space-lattice determines the crystal system.
- (3) The plane passing through **any** three of the nodal points always obeys the law of rational indices, and all parallel planes of atoms are identically constructed and equidistant.
- (4) Only the symmetry of the **holosymmetric (holohedral)** classes is represented by them. The point-systems corresponding to the crystal classes of lower than the full systematic symmetry are not space-lattices, but Sohncke (or Schönflies, Fedorov, and Barlow) point-systems not identical with space-lattices.
- (5) Among the differently inclined (kinds of) planes of atoms of a space-lattice, some are more thickly beset with points than others ; and **those most densely strewn are most widely separated** from their fellow (similar) adjacent parallel planes, and are the **most commonly** and extensively **developed** as faces and are the **most important** (primary and other simple indices) **facial planes** of the crystal, and are also the **planes of cleavage**.

As regards the last part of this fifth attribute, it will be obvious that the planes of atoms parallel to these thickly strewn planes, being most widely separated from each other, and the cohesion being therefore a



minimum (for the whole crystal) between these parallel planes, they can most readily be torn apart to form cleavage surfaces parallel to themselves.

**First Group : Three Space-lattices with Cubic Parallelepiped.**—The elementary parallelepipedon of this group is either (1) a simple cube, with three equal sets of edges corresponding to the three equal and rectangularly intersecting crystallographic

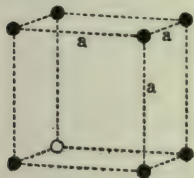


FIG. 452.—Space-lattice 1.

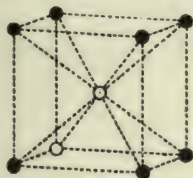


FIG. 453.—Space-lattice 2.

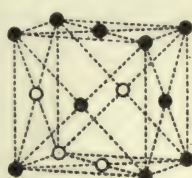


FIG. 454.—Space-lattice 3.

axes  $aaa$ , as represented in Fig. 452; (2) a cube with a point at its centre as shown in Fig. 453; or (3) a cube with a point in the middle of each face, as portrayed in Fig. 454.

The densest packing of points occurs in type (1) along the cube planes, in type (2) along the planes of the rhombic dodecahedron, and in type (3) along those of the octahedron. The faces of the cube, rhombic dodecahedron and octahedron are also the planes of cleavage which alone are developed in cubic crystals, thus agreeing with the rule pointed out in Chapter XXIX. and just emphasised above, that cleavage occurs along those planes in which the points of the structure-lattice are most densely packed. The highly symmetrical nature of these three cubic structures also determines the isotropic or singly refractive optical character of cubic crystals in all directions, the optical properties being represented by a sphere. The absence of double refraction, the main optical distinction of cubic crystals, is thus the direct outcome of the highly symmetrical character of the very simple parallelepipeda of the three cubic space-lattices.

**Second Group : Two Space-lattices with Tetragonal Parallelepiped.**—Two types of space-lattice constitute this group. The elementary parallelepipedon of the one (4) is a simple tetragonal prism, with two kinds of edges,  $a$  the equal and rectangular horizontal ones and  $c$  the vertical ones at right angles to the  $a$  edges, corresponding to the crystallographic axes  $a$  and  $c$ ; and that of the other (5) is a tetragonal prism with a point at its centre. They are shown in Figs. 455 and 456.

The planes of greatest reticular density may be either those of the basal plane or

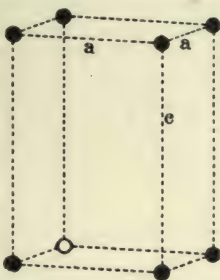


FIG. 455.—Space-lattice 4.

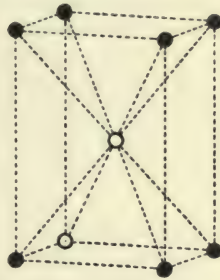


FIG. 456.—Space-lattice 5.

the sides, or the diagonal planes of the prism, or those of the tetragonal pyramid. These correspond to the possible directions of cleavage in the tetragonal system, the principal (tetragonal) axis being the direction of either minimum or maximum cohesion, just as it is the unique direction in the crystal in which optically there is no double refraction and along which the phenomenon of a single optic axis is presented, revealed by the exhibition of a black cross and circular spectrum-coloured rings, when a plate perpendicular to this direction is examined in convergent polarised



light. Both the cohesion and the optical characters are represented by an ellipsoid of revolution, the principal axis of which is the tetragonal axis.

**Third Group: One Space-lattice with Parallelepipeda exhibiting Trigonal-hexagonal Symmetry.**—The elementary parallelepipedon of this group is a simple trigonal prism the section of which is an equilateral triangle having three  $60^\circ$ -angles. Every two such contiguous parallelepipeda, however, are in contact along a prism

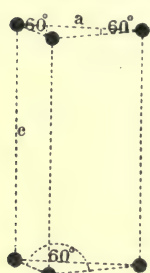


FIG. 457.  
Space-lattice 6.

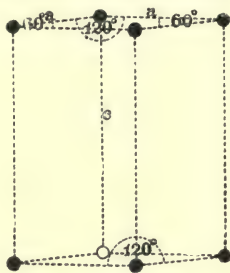


FIG. 458.  
Space-lattice 6.

face of each, which may be considered common, in this space-lattice, and they together make up a rhombic prism of  $120^\circ$  angle. The  $120^\circ$ -prism may, therefore, equally well be considered as the elementary parallelepipedon of this space-lattice No. 6, the points being identical in the two cases. But if the trigonal prism be regarded as the unit parallelepipedon alternate individuals are arranged with their apices inverted. The two prisms are shown in Figs. 457 and 458; Fig. 457 is simply the right half of Fig. 458 with the front and back

points also joined by dotted lines. For we are at liberty to join the two points at the extremities of the narrow diagonal of each rhombic base if we choose. All the horizontal edges of either prism are equal and correspond to the crystallographic Bravais-Miller equal horizontal axes  $a$  of the hexagonal system of symmetry, while the relation of the vertical edges to these is that of the Bravais-Miller axis  $c$ . The plan of such a space-lattice, drawn through the points parallel to the base of the prism, is shown in both Figs. 459 and 460. In Fig. 459 the points are joined by two series of parallel lines inclined at  $120^\circ$ , while in Fig. 460 the same points are shown joined by these two series of lines and also by a third series which we are equally entitled to draw at  $120^\circ$  to the first two series, the three series having equal values as regards the symmetry. It will be obvious that the space-lattice is hexagonal in character, but with a point in the centre of each hexagon; also that the unit parallelepipedon in Fig. 459 has a rhombic base of  $120^\circ$ , corresponding to the rhombic prism of that angle shown in Fig. 458, and that the parallelepipedon of Fig. 460 is the trigonal prism with a  $60^\circ$ -triangle for base as shown in Fig. 457. The homogeneous structure comprised of parallelepipeda each with a simple hexagonal base without a point at its centre is not a space-lattice.

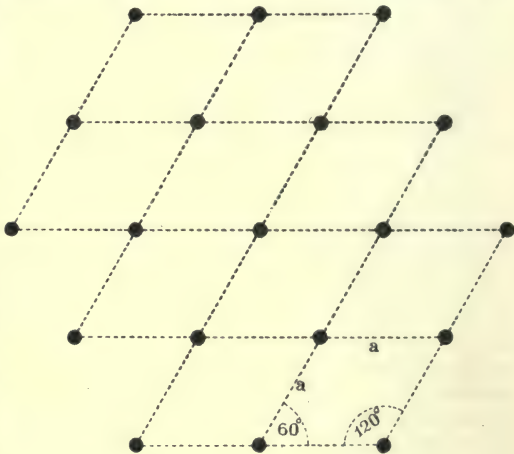


FIG. 459.

If we draw a hexagonal prism, as in Fig. 461, placing a point at the centre of each face of the basal pinakoid, the three horizontal Bravais-Miller hexagonal axes  $a$  will be observed to divide the hexagonal prism up into three rhombic ones of  $120^\circ$  having the same height  $c$ , resembling that of Fig. 458. Hence one is quite

justified in taking the  $120^\circ$ -prism as the elementary parallelepipedon of the space-lattice. But it must be remembered that cleavage parallel to the faces of the hexagonal prism divides the solid up into  $60^\circ$ -triangular prisms, so that we are equally justified on this ground in taking the  $60^\circ$ -prism, the half of the rhombic one, as the unit parallelepipedon of the space-lattice. It will subsequently be shown that in calculating the molecular distance ratios it is immaterial which of the two parallelepipeda is taken as unit, provided it is definitely stated which has been so chosen, and that the same choice is made throughout the whole series of compounds the molecular distance ratios of which are to be compared. For obviously the positions of the points themselves, and the lengths of the lines joining them along the crystallographic axial directions, to which the molecular distance ratios refer, are the same; the volume, however, will be double in the case of the rhombic  $120^\circ$ -prism to what it is in the  $60^\circ$ -prism, so that the absolute values of the distance ratios will be different, although their ratio will be the same, namely, that of the crystallographic axial ratio  $a : c$ .

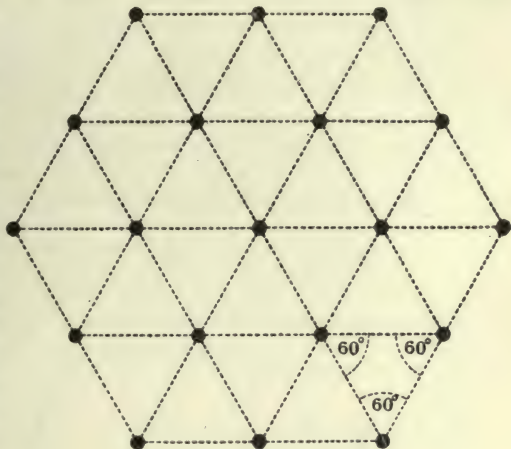


Fig. 460.

In this space-lattice the greatest reticular density may be along the basal plane of the prisms, or along the three planes mutually inclined at  $120^\circ$  intersecting in the prism axis and perpendicular to the basal plane. Thus the axial direction of the prism is a direction of optical single refraction and of minimum or maximum cohesion, and the principal axis of the ellipsoids of revolution which represent respectively the optical properties and the cohesion. Hexagonal or trigonal crystals constructed according to this space-lattice are, therefore, uniaxial like tetragonal crystals as regards their optical behaviour. Perfect cleavage may occur either parallel to the basal plane or to the faces of the hexagonal prism. Secondary cleavage may also occur, however, parallel to the faces of a hexagonal pyramid,

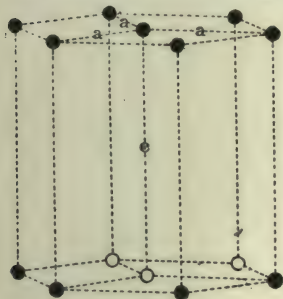


Fig. 461.

as the plane passing through any pair of points in the basal plane and the opposite point at the other end of the same trigonal prism concerned is also one which is comparatively thickly strewn with points.

**Fourth Group: One Space-lattice with Trigonal-rhombohedral Parallelepipedon.**—Like the third group, only one space-lattice No. 7 is comprised in this group, the elementary parallelepipedon of which is the rhombohedron. It is represented in Fig. 462.

It possesses three planes of symmetry which intersect each other regularly, that is, at  $60^\circ$ , in the vertical or principal axis, the trigonal axis. The three edges of the parallelepipedon are equal, corresponding to the three equal Millerian axes  $a$ , and are equally inclined to each other; but the rhombohedral angle is different for

different substances. The vertical principal axis (not a Millerian axis) is a direction of single refraction, just as is the trigonal axis of a trigonal prism belonging to space-lattice 6, and it is also the principal (or singular) axis of the ellipsoid of revolution which expresses the optical characters. Thus, like the tetragonal and hexagonal parallelepipeda, the rhombohedron is optically uniaxial. The points may be most thickly strewn either along the faces of the rhombohedron, in which case cleavage occurs along these planes, as in calcite for instance, or along planes perpendicular to the principal (vertical) axis, when the cleavage follows the direction of the basal plane; or else, thirdly, along the three symmetry planes or their bisecting planes, all of which intersect in the principal axis, and either of which confers cleavage parallel to the faces of a hexagonal prism.

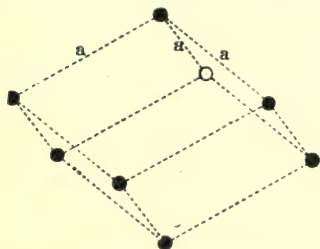


FIG. 462.—Space-lattice 7.

**Fifth Group : Four Space-lattices with Orthorhombic Parallelepipeda.**—This group comprises four parallelepipeda which are symmetrical to three mutually rectangular planes. They are represented in Figs. 463, 464, 465, and 466. The first, that of space-lattice No. 8, is a rhombic prism with normal base

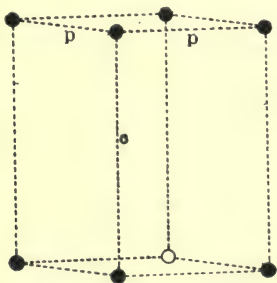


FIG. 463.—Space-lattice 8.

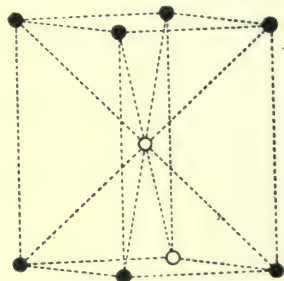


FIG. 464.—Space-lattice 9.

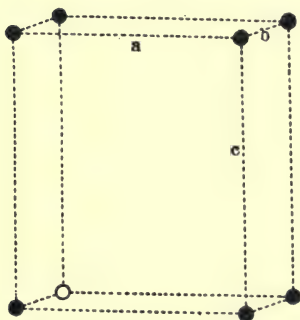


FIG. 465.—Space-lattice 10.

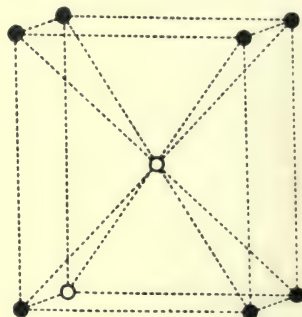


FIG. 466.—Space-lattice 11.

(perpendicular to the axis of the prism); the prism faces correspond to those of the crystallographic form  $\{110\}$ , and the basal edges are therefore marked  $p$  in Fig. 463, while the vertical edges correspond to the axis  $c$ , to which they are parallel. The second, that of space-lattice No. 9, is the same but with a point at the centre, forming a rhombic pyramid with the four points at the base. The third, that of space-lattice No. 10,



is the right-rhombic prism, a rectangular parallelepipedon with three unequal sets of edges parallel to the crystallographic axes  $a$ ,  $b$ , and  $c$ . The fourth, that of space-lattice No. 11, is the same as the last but with a point at the centre forming a right rhombic pyramid with the four basal points. The optical ellipsoid must here be obviously one with three unequal rectangular axes, the lines of intersection of the three rectangularly intersecting symmetry planes, and there will be no longer one predominating singular axis, that of an ellipsoid of revolution and the unique direction of single refraction, but there will be a pair of directions of single refraction, those two perpendicular to which the ellipsoid of general form will have circular sections, of radius equal to the intermediate axis and of which the latter is a common diameter. The crystals are, therefore, said to be optically biaxial, and a plate perpendicular to the acute bisectrix of the angle between these two optic axes (directions of single refraction, and not to be confounded with the three axes of the optical ellipsoid, two of which bisect the acute and obtuse angles between the optic axes) actually shows their positions when examined in convergent polarised light. For these positions are marked by a series of concentric (confocal) spectrum-rings, like Newton's rings, in each case, but which are lemniscates and not true circles; the two centres

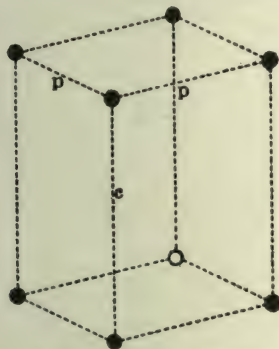


FIG. 467.—Space-lattice 12.

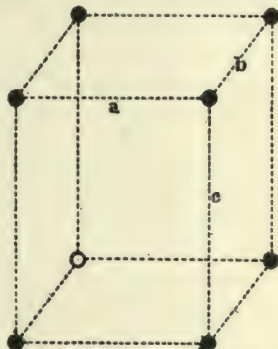


FIG. 468.—Space-lattice 13.

or foci where the optic axes are located are further marked by the sharply defined apices of dark hyperbolic curves ("brushes"), which join up to form a black cross when the symmetry planes coincide with the planes of the Nicol prisms of the polariscope, one arm of the cross passing through both optic axes and the other crossing this first arm rectangularly midway between the two optic axes (see Fig. 686, Plate V., for aragonite). In space-lattices Nos. 8 and 9 the symmetry planes are the basal plane and the two planes containing the diagonals of the rhombic base and the vertical axis; in space-lattices Nos. 10 and 11 they are the planes parallel to the prismatic and basal pinakoid faces. Owing to the variable dimensions of the three sets of rectangular edges and of the pyramidal angle, the planes most densely strewn with points may be (1) one of the three planes of symmetry, (2) the planes of the rhombic prism, or (3) those of the rhombic pyramid; consequently, three corresponding varieties of cleavage can occur.

**Sixth Group : Two Space-lattices with Monoclinic Parallelepipeda.**—This group comprises two types of parallelepipeda, namely, (1) the rhombic prism with inclined base, Fig. 467, which builds up space-lattice No. 12, and corresponds to the monoclinic prism  $\{110\}$  closed by the basal pinakoid  $\{001\}$ , the basal edges being consequently marked  $p$  in the figure, and the vertical prism edges  $c$  (being parallel to the axis  $c$ ); and (2) the parallelepipedon with two pairs of rectangular faces (oblongs) and one pair of oblique (rhomboidal) ones, which may be regarded as a rectangular rhombic prism

which has been pushed over along one of its three planes and corresponds to the solid formed by the combination of the three monoclinic pinakoids, the basal pinakoid  $\{001\}$ , ortho-pinakoid  $\{100\}$ , and clino-pinakoid  $\{010\}$ , the latter oblique pair of faces being parallel to the symmetry plane. The edges of this second type are thus parallel to the crystallographic axes  $a$ ,  $b$ , and  $c$ ; it is shown in Fig. 468, and builds up the space-lattice No. 13. Both types possess only one symmetry plane, the unique one characterising the monoclinic system, passing through the front and back points in Fig. 467, but parallel to the right and left sides of the prism of Fig. 468.

The planes of greatest density of points may be the faces of the prism in Fig. 467, or any other two planes symmetrical to the symmetry plane, or there may be only one plane of maximum density, either parallel or perpendicular to the symmetry plane. The cleavage will follow these directions. Optically, the crystals are characterised by an ellipsoid with three unequal axes, and consequently possess two optic axes of single refraction, like the fifth rhombic group, the only difference being that the ellipsoid is now only fixed in direction as regards that axis which is perpendicular to the symmetry plane, whereas in group five the three axes of the ellipsoid are all identical with the three structural and crystallographic axes.

**Seventh Group : One Space-lattice with Triclinic Parallelepiped.**—This is the general case of a space-lattice, No. 14, the elementary parallelepipedon of which is of

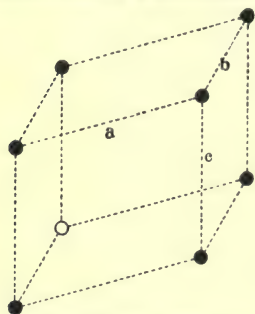


FIG. 469.—Space-lattice 14.

triclinic character, that is, the three sets of edges parallel to the crystallographic axes  $a$ ,  $b$ ,  $c$  are of unequal length and their three angles of inclination  $\alpha$ ,  $\beta$ , and  $\gamma$  are also unequal. It is shown in Fig. 469. These six elements for any one substance are different from those of any other substance which crystallises according to this same type of structure. The three planes of the three pairs of faces thus correspond to the three triclinic pinakoids, which combine to form the simple closed solid of the triclinic system the faces of which are parallel to the crystallographic axial planes, namely, the basal pinakoid  $\{001\}$ , the macro-pinakoid  $\{100\}$ , and the brachy-pinakoid  $\{010\}$ . Any plane of points, however, may have the greatest reticular density, and the cleavage

is thus subject to no definite rule, beyond the fact that only one plane can be that of perfect cleavage, perpendicular to the unique direction of minimum cohesion, there being no symmetry other than centric developed. Optically, a similar ellipsoid with three unequal axes and having two optic axes or directions of single refraction characterises the structure, as in the cases of the rhombic and monoclinic groups; but there is now no restriction whatever as to its position. Actual observation has shown, however, that when a plane of perfect cleavage is developed in a triclinic crystal, one of the axes of the optical ellipsoid is as a rule nearly perpendicular to it, and the other two axes are nearly parallel to it. The same curious occurrence is often observed also in the monoclinic system, where, when a perfect cleavage is developed parallel to a plane perpendicular to the symmetry plane, one of the axes of the optical ellipsoid is frequently nearly perpendicular to it. Mica is an excellent example, the cleavage of which, the most perfect of that of all known crystals, is so nearly perpendicular to that axis of the optical ellipsoid which forms the bisectrix of the acute angle between the two optic axes (directions of single refraction) that the well-known interference figure of rings and brushes, above described as characteristic of biaxial crystals when a suitable plate is examined in convergent polarised light, is exhibited to perfection by a cleavage plate of mica; the two series of spectrum-coloured rings surrounding the two optic axes are apparently (although careful measurement shows that they are not absolutely) symmetrical to the centre of the field of the polariscope (see Figs. 676 and 677 on Plate IV., interference figures of mica).



**Molecular Distance Ratios or Topic Axial Ratios.**—Having now described the fourteen space-lattices, the points of which represent the molecular or polymolecular grosser structural units and the elementary parallelepipeda of which represent the molecular or polymolecular cells, we are in a position to discuss the mode of combining the crystallographic axial ratios with the molecular volume, so as to represent the relative directional dimensions of the parallelepipeda for a definitely related isomorphous series of substances, the differences between these dimensions for the different members of the series corresponding to the total change of molecular volume which occurs when one of the interchangeable chemical elements is replaced by another. The genesis of the constants is due to three distinct investigators, Prof. F. Becke of Prague, who suggested the idea,<sup>1</sup> Prof. W. Muthmann of Munich,<sup>2</sup> and the author,<sup>3</sup> who simultaneously and quite unknown to each other applied it in practical investigation, the former in the case of the permanganates of the alkalis, and the latter to the alkali sulphates and subsequently to the corresponding selenates and to the double sulphates and selenates. These dimensional constants were termed by the author "distance ratios," and by Muthmann "topic axial ratios," from *τόπος*, "space." The ratios really represent the relative distances apart of the points of the space-lattice—the centres of gravity or other analogous representative points (such as a particular atom of every molecule or group of molecules) of contiguous chemical molecules or polymolecular crystal units—in the directions of the crystallographic axes, that is, the dimensions of the elementary parallelepipedon or molecular (or polymolecular) cell, and not the actual dimensions of the material molecule or group of molecules itself. For we do not yet know the relations of the free space and the actual matter in the unit cell or elementary parallelepipedon of the space-lattice corresponding to each molecule or polymolecular group. Further consideration and the later development of the work in this domain only confirm the author's original view that the term "molecular distance ratios" is the most suitable appellation for these important constants. Muthmann's term "topic axial ratios," however, has come more generally into use.

It is now definitely proved that the structural units of the space-lattice, the chemical molecules or polymolecular crystal-units, of the various members of any one and the same isomorphous series are built up into crystals on the same plan. The elements of the crystals, which it will be remembered are the relative lengths of the crystallographic axes  $a$ ,  $b$ , and  $c$  cut off by the primary (parametral) pyramid faces and the three mutual inclinations of the axes  $\alpha$ ,  $\beta$ , and  $\gamma$ , are consequently relative measures of the sides and also the angles of the elementary parallelepipedon of the structure. The axial ratios, being usually expressed so that  $b = 1$ , only afford the mutual relations of the three axes to each other in that particular substance, and give no idea of the relations between the dimensions of the elementary parallelepipeda of different members

<sup>1</sup> *Anzeiger der kais. Akad. der Wiss.*, Wien, 1893, 30, 204.

<sup>2</sup> *Zeitschr. für Kryst.*, 1894, 22, 497.

<sup>3</sup> *Journ. Chem. Soc. Trans.*, 1894, 65, 628.



of the series. But if we take the relative volumes of the parallelepipeda into consideration, by combining the molecular volume of each member of the series with its crystallographic elements, we at once obtain the relative dimensions of the elementary parallelepipeda of the various members of the series. These three new axial dimensions expressing the true relations in space are the **molecular distance ratios or topic axial ratios**, and are represented by  $\chi$ ,  $\psi$ , and  $\omega$ .

They are expressed by simple formulæ involving only the crystallographic axial values  $a$ ,  $b$ ,  $c$  and the axial angles  $\alpha$ ,  $\beta$ ,  $\gamma$ , the density (specific gravity at  $20^\circ$  compared with water at  $4^\circ$ ) of the crystals, and the molecular weight of the chemical substance composing the crystal. If the whole space of the elementary parallelepipedon were filled with the matter of the molecule or small group of molecules, that is, if the various atoms were packed in contact without interstices and the whole filled and took the shape of the parallelepipedon, the molecular distance ratios would indicate the relative dimensions of the chemical molecules themselves. For even if the crystal-unit comprise more than one molecule (as is often the case, *e.g.* the alkali sulphates), there are the same number of molecules per crystal-unit for all the isomorphous substances compared; hence the relative values are equally well expressed by ignoring that

number, a procedure which is only equivalent to dividing out the values for all the salts of the series by that same number. But it is certain that the molecular or polymolecular cell is not thus filled with matter, hence, as above indicated, they do not represent the molecular or polymolecular dimensions but the distances apart of the molecular or group-crystal-unit representative points along the directions of the axes. It is very important that this distinction should be thoroughly understood, as the designation "topic axial ratios" does not fully imply it, and it is for this specific reason that the term "molecular distance ratios" is more appropriate.<sup>1</sup>

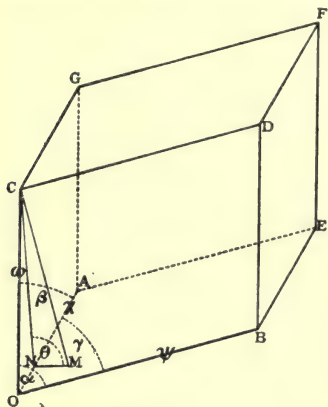


FIG. 470.

In order to derive the formulæ the most general case, that of a triclinic crystal, space-lattice No. 14, will first be considered, and subsequently the formulæ will be shown to simplify, stage by stage, as the symmetry ascends.

In the triclinic parallelepipedon shown in Fig. 470 (an enlarged Fig. 469) the axial angles are  $\alpha$ ,  $\beta$ , and  $\gamma$ , and the lengths of the sides  $OA$ ,  $OB$ , and  $OC$  are  $\chi$ ,  $\psi$ , and  $\omega$ .

<sup>1</sup> V. M. Goldschmidt (*Zeitschrift für Kryst.*, 1912, 51, 25) considers the topic axes as lengths, expressed in centimetres, of the sides of a parallelepipedon of such a size that it has the weight of a gram-molecule (molecular weight in grammes). For they contain the factor  $\sqrt[3]{V}$ , of the dimension  $\text{cm.}^1$ ,  $V$  being the volume of the gram-molecule in  $\text{cm.}^3$ .

If we let fall a perpendicular CM from the corner C on to the face AOBE, and from M draw MN perpendicular to OA, and call the angle CNM (between the planes AOB and AOC)  $\theta$ , then V, the volume of the parallelepipedon, is expressed by the formula :<sup>1</sup>

$$V = \chi \psi \omega \sin \beta \cdot \sin \gamma \cdot \sin \theta.$$

Now  $\chi$ ,  $\psi$ , and  $\omega$  bear the same relation to each other as do the axial ratios  $a : b : c$ , so that :

$$a = \frac{\chi}{\psi}, \text{ and } c = \frac{\omega}{\psi}.$$

Hence :

$$\begin{aligned} \chi &= a\psi, \text{ and } \omega = c\psi, \text{ and} \\ V &= a\psi \cdot \psi \cdot c\psi \sin \beta \cdot \sin \gamma \cdot \sin \theta, \\ &= ac\psi^3 \cdot \sin \beta \cdot \sin \gamma \cdot \sin \theta, \end{aligned}$$

or

$$\psi^3 = \frac{V}{ac \sin \beta \cdot \sin \gamma \cdot \sin \theta}$$

and

$$\psi = \sqrt[3]{\frac{V}{ac \sin \beta \cdot \sin \gamma \cdot \sin \theta}}.$$

Then :

$$\chi = a\psi = \sqrt[3]{\frac{a^2 V}{c \sin \beta \cdot \sin \gamma \cdot \sin \theta}}$$

and

$$\omega = c\psi = \sqrt[3]{\frac{c^2 V}{a \sin \beta \cdot \sin \gamma \cdot \sin \theta}}.$$

It may happen that the angle  $\theta$  has not been calculated during the ordinary calculation of the elements  $a : b : c$  and  $\alpha$ ,  $\beta$ ,  $\gamma$ , and the crystal angles. In this event it may readily be derived from the following formula of the well-known type :

$$\sin \frac{\theta}{2} = \sqrt{\frac{\sin(s-\beta) \sin(s-\gamma)}{\sin \beta \sin \gamma}},$$

where

$$s = \frac{a + \beta + \gamma}{2}.$$

The molecular distance ratios are finally expressed in a similar manner to the crystallographic axial ratios, namely, as  $\chi : \psi : \omega$ .

The above expressions for the relative values of the molecular distance ratios  $\chi$ ,  $\psi$ , and  $\omega$  in the general case of a triclinic crystal simplify with the introduction of symmetry, the first stage being obviously that of the monoclinic system.

In the case of a **monoclinic** crystal of analogous axial-plane-pinakoidal type, constructed according to space-lattice No. 13, Fig. 468, the angles  $\alpha$ ,  $\gamma$ , and  $\theta$  are right angles, and as  $\sin 90^\circ = 1$  we have :

$$\chi = \sqrt[3]{\frac{a^2 V}{c \sin \beta}}, \quad \psi = \sqrt[3]{\frac{V}{ac \sin \beta}}, \quad \omega = \sqrt[3]{\frac{c^2 V}{a \sin \beta}}.$$

When the symmetry is **rhombic**, the structure being that of the rectangular axial-plane type of space-lattice No. 10, Fig. 465,  $\beta$  is also  $90^\circ$ , and  $\sin \beta$  also consequently disappears, so that :

$$\chi = \sqrt[3]{\frac{a^2 V}{c}}, \quad \psi = \sqrt[3]{\frac{V}{ac}}, \quad \omega = \sqrt[3]{\frac{c^2 V}{a}}.$$

These formulæ were given by the author in the 1894 memoir already alluded to, and the monoclinic formulæ in a succeeding one in the year 1896.

In the case of **tetragonal** symmetry, corresponding to space-lattice No. 4, Fig. 455,  $a = b = 1$ , so that :

$$\chi = \psi = \sqrt[3]{\frac{V}{c}}, \text{ and } \omega = \sqrt[3]{c^2 V}.$$

When, finally, the symmetry of the cubic system is reached, and the structure is

<sup>1</sup> Kraus and Mez, *Zeitschrift für Kryst.*, 1901, 34, 390.

the simple cubic one of space-lattice No. 1, Fig. 452,  $a=b=c=1$ , so that obviously  $\chi=\psi=\omega=\sqrt[3]{V}$ .

The formulæ for the **trigonal system** may also be derived directly from the general triclinic ones. We have in this case the trigonal space-lattice No. 7, Fig. 462, in which the conditions are that:  $a=b=c=1$  and  $\alpha=\beta=\gamma$ , so that the general formulæ reduce to:

$$\chi=\psi=\omega=\sqrt[3]{\frac{V}{\sin^2 a \sin \theta}},$$

$\theta$  in this case being the inner angle over the polar edges of the rhombohedron, the supplement of the outer angle actually measured between two faces of the rhombohedron over their intersecting polar edge. Its relation to the crystal element  $a$  is expressed by the simple formula

$$\sin \frac{\theta}{2} = \frac{\sin \frac{a}{2}}{\sin a}.$$

The case of **hexagonal symmetry** is peculiar, for it has already been shown that in a hexagonal space-lattice, owing to the fact that a point also occupies the centre of each hexagon, the points are situated at the corners of a  $120^\circ$ -prism, which may be considered as the base of the elementary parallelepipedon; every three such prisms together make up the hexagonal prism, as will be clear from Fig. 458 already given showing the simple prism, Fig. 461 showing the combination of three to make up the hexagonal prism, and Fig. 471 now given to show the basal plan of the three.

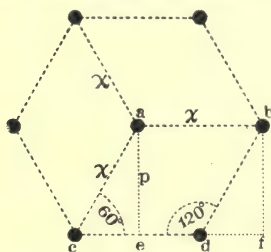


FIG. 471.

Assuming then that the  $120^\circ$ -prism is the elementary parallelepipedon, the molecular distance ratio  $\chi:\omega$  is calculated in the following manner. The relation between the common height of the prisms  $\omega$  and the distance  $\chi$  separating the points in the horizontal plane (the sides of the rhombic base), employing Bravais-Miller axes, is that of the vertical axis  $c$  to any one of the three horizontal axes  $a$ , that is, it is equal to the crystallographic axial ratio  $a:c$ , or as  $a=1$  it is equal to  $c$ ; hence  $\frac{\omega}{\chi}=c$ . All three horizontal axes being equal, we refer to them indifferently as  $\chi$ .

Now, if  $p$  in Fig. 471 represent the perpendicular  $ae$  from the centre on one of the sides  $cd$  of the hexagon,  $p=\chi \sin 60^\circ$ , and the volume  $V$  of the  $120^\circ$ -prism is afforded by multiplying the height  $\omega$  into the area  $p\chi$  of the rectangle  $abfe$ , as this rectangle is equal to the base  $abdc$  of the  $120^\circ$ -prism. Therefore,

$$\begin{aligned} V &= \omega \cdot \chi^2 \sin 60^\circ, \\ &= c\chi \cdot \chi^2 \sin 60^\circ, \\ &= c\chi^3 \sin 60^\circ. \end{aligned}$$

Hence,

$$\chi^3 = \frac{V}{c \sin 60^\circ}, \text{ and } \chi = \sqrt[3]{\frac{V}{c \sin 60^\circ}}.$$

Also, as

$$\omega = c\chi, \text{ and } \omega^3 = c^3\chi^3 = \frac{c^2V}{\sin 60^\circ},$$

we have

$$\omega = \sqrt[3]{\frac{c^2V}{\sin 60^\circ}}.$$

These simple formulæ for  $\chi$  and  $\omega$  thus represent the molecular distance ratio on the assumption that the  $120^\circ$ -prism is the elementary parallelepipedon. But it has also been shown that the half of this, the  $60^\circ$ -prism, is equally entitled, from the point



of view of the cleavage, to be considered as the elementary parallelepipedon. If this assumption be made the ratio  $\chi : \omega$  will still have the same value, that of the crystallographic axial ratio  $a : c$ , but the absolute numbers themselves and the formulæ expressing them will be different, on account of the volume now being only one-half of that of the  $120^\circ$ -prism. The points  $a$  and  $d$  must be supposed to be joined in Fig. 471, and the area of the base  $acd$  of the  $60^\circ$ -prism will be  $p\frac{\chi}{2}$  instead of  $p\chi$ .

The volume  $V$  is, therefore, as under :

$$\begin{aligned} V &= \omega \cdot p\frac{\chi}{2} = \omega \cdot \chi \sin 60^\circ \cdot \frac{\chi}{2} = \frac{1}{2}\omega\chi^2 \sin 60^\circ, \\ &= \frac{1}{2}c\chi \cdot \chi^2 \sin 60^\circ = \frac{c\chi^3 \sin 60^\circ}{2}, \end{aligned}$$

and

$$\chi^3 = \frac{2V}{c \sin 60^\circ},$$

from which

$$\chi = \sqrt[3]{\frac{2V}{c \sin 60^\circ}}.$$

Then

$$\omega = c\chi, \quad \omega^3 = \frac{2Vc^3}{c \sin 60^\circ} = \frac{2c^2V}{\sin 60^\circ},$$

and

$$\omega = \sqrt[3]{\frac{2c^2V}{\sin 60^\circ}}.$$

Thus the formulæ for  $\chi$  and  $\omega$ , on the assumption that the  $60^\circ$ -prism is the elementary parallelepipedon, only differ from those for a  $120^\circ$ -prism parallelepipedon by having an additional figure 2 in the numerator of the expression in each case. In the above alternative cases for the treatment of hexagonal crystals it has thus been assumed that the molecular cell, corresponding to a chemical molecule (or poly-molecular crystal-unit) of the substance, is either the  $120^\circ$ -prism or the  $60^\circ$ -prism, with normal base in each case, each point of the space-lattice representing a molecule (or group of molecules) just as in the case of the simplest of all space-lattices, the cubic No. 1; in fact the  $120^\circ$ -prism may be regarded as a cubic one pushed over  $30^\circ$  laterally in one direction and elongated or compressed vertically according to the value of the vertical axis  $c$ .

We have now dealt with the calculation of the molecular distance ratios for the elementary parallelepipeda of the seven simplest space-lattices, one corresponding to each of the seven crystalline systems. These will be the cases most frequently required.

Two other cases of great importance and also often required are those of the rhombic and monoclinic space-lattices Nos. 8 (Fig. 463) and 12 (Fig. 467) respectively, in both of which the base is a rhombic prism and the volume of the prismatic parallelepipedon is one-half of that of the parallelepipedon with rectangular base (space-lattices Nos. 10 and 13, Figs. 465 and 468) the edges of which are parallel to the crystallographic axes  $a$  and  $b$ . These two cases, in fact, resemble the one just dealt with, in which the  $60^\circ$ -prism has one-half the volume of the  $120^\circ$ -prism, and the formulæ can be shown to differ in the same simple manner from those for the parallelepipedon of double the volume, namely, by the addition of a 2 in the numerator in each case.

The case of the **rhombic space-lattice, No. 8**, the elementary parallelepipedon of which is shown in Fig. 463, may well be taken as an example of the mode of deriving the formulæ. It has been shown by Barker<sup>1</sup> to be the structure present in the barytes group of minerals and in the perchlorates and permanganates of the alkalis (the latter having been investigated by Muthmann<sup>2</sup>). The directions of perfect

<sup>1</sup> *Journ. Chem. Soc. Trans.*, 1906, 89, 1141.

<sup>2</sup> *Zeitschr. für Kryst.*, 1894, 22, 497.

cleavage are parallel to the basal plane {001} (highly perfect) and the orthorhombic prism {110}, precisely the planes of the space-lattice and those along which the reticular density is greatest. The case of these salts is thus a very clear and indeed unmistakable one. The plan of such a prism is shown in Fig. 472, which also

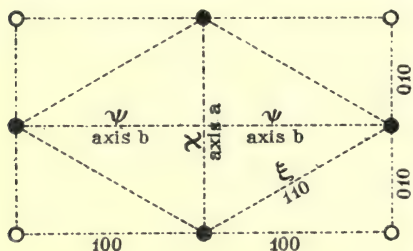


FIG. 472.

exhibits for comparison the points of the rectangular rhombic space-lattice No. 10, these latter points being shown as rings to distinguish them. It will at once be clear that the area of the rhombic base (solid points) is one-half of that of the base of the rectangular rhombic prism the edges of which are parallel to the horizontal axes  $a$  and  $c$ ; and as the volume = area  $\times$  height, the volume is also one-half, the height being common. The axes  $a$  and  $b$  are the diagonals of the rhombic prism, and the

diagonal molecular distances  $\chi$  and  $\psi$  respectively. The vertical distance between the points, corresponding to the common height of the prisms, is as usual called  $\omega$ . Besides these molecular distances we have also to consider a fourth important dimension, namely, the side of the prism, which we may call molecular distance  $\xi$ . Now, the volume  $V$  of the rhombic prism is obviously

$$V = \frac{1}{2} \chi \cdot \psi \cdot \omega,$$

if we consider that of the rectangular rhombic prism as the product of the three molecular distances  $\chi$ ,  $\psi$ ,  $\omega$ . As  $\omega = c\psi$  and  $\chi = a\psi$ , from the fundamental assumption that the molecular distance ratios bear the same relation to each other as do the crystallographic axial ratios, being in fact the structural expression of the latter, we may substitute these values for  $\chi$  and  $\omega$  in the expression for the volume, and thus get :

$$V = \frac{1}{2} a\psi \cdot \psi \cdot c\psi, \\ = \frac{1}{2} ac\psi^3.$$

Hence : 
$$\psi^3 = \frac{2V}{ac}, \text{ and } \psi = \sqrt[3]{\frac{2V}{ac}}.$$

Then : 
$$\chi = a\psi,$$

and : 
$$\chi^3 = \frac{2a^3V}{ac} = \frac{2a^2V}{c}, \text{ from which } \chi = \sqrt[3]{\frac{2a^2V}{c}}.$$

Also : 
$$\omega = c\psi,$$

and : 
$$\omega^3 = \frac{2c^3V}{ac} = \frac{2c^2V}{a}, \text{ from which } \omega = \sqrt[3]{\frac{2c^2V}{a}}.$$

The fourth molecular dimension,  $\xi$  the side of the rhombic base and edge (001) : (110), is at once afforded by the following simple considerations :

$$\xi^2 = \left(\frac{\chi}{2}\right)^2 + \left(\frac{\psi}{2}\right)^2 = \frac{1}{4}(\chi^2 + \psi^2).$$

Putting in the values of  $\chi$  and  $\psi$  already found, and simplifying, we have :

$$\xi^2 = \frac{1}{4} \left[ \left( \sqrt[3]{\frac{2a^2V}{c}} \right)^2 + \left( \sqrt[3]{\frac{2V}{ac}} \right)^2 \right] = \frac{1}{4}(1 + a^2) \left( \sqrt[3]{\frac{2V}{ac}} \right)^2,$$

$$\xi = \frac{1}{2} \sqrt{1 + a^2} \cdot \sqrt[3]{\frac{2V}{ac}}.$$

Intimately connected at the same time with this case of the space-lattice having for its elementary parallelepipedon a prism with rhombic base, and with the case previously treated of the hexagonal space-lattice which has the 120°-prism for its unit molecular cell, is the very important case of the numerous **pseudo-hexagonal crystals**. Our

typical crystallised substance potassium sulphate is a particularly striking example of this case, as already mentioned in Chapter XXVIII, p. 511, as are also the whole of the salts of the very important isomorphous series of alkali sulphates and selenates of which it forms the first and best-known member. Fig. 417 on p. 512 shows, for instance, a crystal of rubidium sulphate closely resembling a hexagonal bipyramid modified round the basal edges by short faces of the hexagonal prism. The treatment of the pseudo-hexagonal problem will, therefore, be next worked out for this series of rhombic salts,  $R_2SeO_4$ , and the formulæ arrived at shown to be of general application to the case.

It has been shown by the author that the prism zone of these alkali sulphates and selenates, consisting of the two parallel brachy-pinakoid faces  $b = \{010\}$  and the four faces of the primary prism  $p = \{110\}$ , approaches a hexagonal prism so closely that the angles are within  $1^\circ$  of  $60^\circ$ . In the case of our typical crystal of potassium sulphate itself, the angles were shown in Chapter IV. to be  $bp = (010) : (110) = 60^\circ 12'$ , and  $pp = (110) : (\bar{1}\bar{1}0) = 59^\circ 36'$ . The former is four times symmetrically repeated in the zone, and the latter twice, the six angles together making up  $360^\circ$ . The variation is but small for the different members of the series (see table of angles on page 382),  $pp$  varying only from  $59^\circ 22'$  to  $59^\circ 38'$  in the more strictly comparable sulphates and selenates containing potassium, rubidium, or caesium. Now the cleavage directions common to the whole of the metallic salts of this isomorphous series are the brachy-pinakoid  $b = \{010\}$  and the basal pinakoid  $c = \{001\}$ ; both are good cleavages, but the former is the more perfect of the two in the cases of the potassium, rubidium, caesium, and thallium salts, while in the case of ammonium sulphate, doubtless owing to the stereometric difference between a metal and the radicle group  $NH_4$ , the latter cleavage is very perfect while the former is not developed at all. The absence throughout the series of any cleavage parallel to the macro-pinakoid  $a = \{100\}$  fully agrees with the assumption that the structure is not of a rectangular rhombic character, and the actual cleavages developed are quite in accordance with a pseudo-hexagonal structure, in which the basal pinakoid and the brachy-pinakoid are planes thickly strewn with points, whereas the plane of the macro-pinakoid, which would be the third plane of a rectangular rhombic structure, is not.

The conditions will be appreciated with the aid of Fig. 473, which is reproduced from the author's memoir on "topic axes, and the topic parameters of the alkali sulphates and selenates."<sup>1</sup> The crystal is supposed to be rotated  $90^\circ$  about the vertical axis, from the usual position of representation of a rhombic crystal, so as to bring it into the position corresponding to the normal hexagonal prism, usually referred to as of the first order, and to the hexagonal space-lattice as shown in Fig. 471. Indeed Fig. 473 may be taken to represent either the arrangement of points in the space-lattice, or the plan of a hexagonal prism or hexagonal pyramid. In the case of the alkali sulphates and selenates the hexagonal prism (here not absolutely hexagonal but pseudo) is built up of the two faces of  $b = \{010\}$  and the four faces of  $p = \{110\}$  as already mentioned, while the corresponding pyramid is built up of the four primary pyramid faces  $o = \{111\}$  and the pair of brachy-dome faces  $q' = \{021\}$ .

In Fig. 473  $\chi, \psi, \omega$  represent the molecular distances on the assumption of pseudo-hexagonal structure, while  $\chi', \psi', \omega'$  refer to a rectangular rhombic structure, these latter topic axes being parallel to the crystallographic axes.

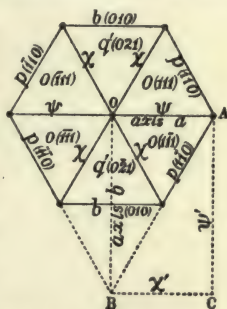


FIG. 473.—Pseudo-hexagonal Space-lattice of Alkali Sulphates and Selenates.

<sup>1</sup> *Journ. Chem. Soc. Trans.*, 1905, 87, 1185.



The vertical crystallographic axis  $c$  is equally coincident with the vertical topic axis  $\omega$  or  $\omega'$  on either assumption, and is not actually shown in the figure as it is perpendicular to the plane of the paper. The direction OA of the crystallographic axis  $a$  is that of the pseudo-hexagonal topic axis  $\psi$  or of the rectangular rhombic topic axis  $\chi'$ . The direction OB of the crystallographic axis  $b$  is that of the rectangular rhombic topic axis  $\psi'$ , but is no longer a topic axial direction on the assumption of a pseudo-hexagonal space-lattice; instead, we have a pair of equal pseudo-hexagonal topic axes  $\chi$ , which, as the lattice is not perfectly hexagonal, are not quite equal in length to the topic axis  $\psi$ . Now, it will at once be seen on comparing Fig. 472, representing the structure with a rhombic base, with Fig. 473 that the  $\chi$  of Fig. 472 is the  $\psi$  of Fig. 473, and that the pair of molecular distances  $\chi$  of Fig. 473 correspond to  $\xi$ , the side of the rhombic base in Fig. 472. Also, the vertical topic axis is common. Hence, if  $V$  represent the molecular volume and  $a$  and  $c$  the crystallographic axial ratios as usual, the pseudo-hexagonal molecular distance ratios are as under :

$$\begin{aligned}\chi &= \frac{1}{2}\sqrt{1+a^2}\sqrt{\frac{3}{2V}}\sqrt{\frac{2V}{ac}}, \\ \psi &= \sqrt{\frac{3}{2a^2V}}\sqrt{\frac{2V}{c}}, \\ \omega &= \sqrt{\frac{3}{2c^2V}}\sqrt{\frac{2V}{a}}.\end{aligned}$$

This may be directly proved from first principles as follows. The area of the rhombus the sides of which are  $\chi$  is obviously half the area of the rectangle  $\chi'\psi'$ ;  $\psi$  is equal to the shorter diagonal of the rhombus parallel to the axis  $a$ , and the longer diagonal is the axis  $b$ . Now, the elementary parallelepipedon has the rhombus for its base and  $\omega$  for its height (parallel to the axis  $c$ ). Hence, expressing the volume in terms of the rectangular rhombic topic axes :

$$V = \frac{1}{2}\chi' \cdot \psi' \cdot \omega', \quad (1).$$

But as the sides of this rectangular parallelepipedon are proportional to the crystallographic axes :

$$\chi' : \psi' : \omega = a : 1 : c,$$

and, remembering that the two vertical topic axes  $\omega$  and  $\omega'$  are identical :

$$\chi' = \frac{a\omega}{c}, \quad (2); \text{ and } \psi' = \frac{\omega}{c}, \quad (3).$$

Substituting these values in (1) we obtain :

$$V = \frac{1}{2} \cdot \frac{a\omega}{c} \cdot \frac{\omega}{c} \cdot \omega = \frac{a\omega^3}{2c^2}.$$

From which we derive :

$$\omega^3 = \frac{2c^2V}{a}, \text{ and } \omega = \sqrt[3]{\frac{2c^2V}{a}}.$$

As regards  $\psi$  it has been shown to be equal to  $\chi'$ ; therefore, from (2) :

$$\psi = \frac{a}{c} \cdot \sqrt[3]{\frac{2c^2V}{a}} = \sqrt[3]{\frac{2a^2V}{c}}.$$

As regards  $\chi$ , it will be apparent that :

$$\chi^2 = \left(\frac{\psi}{2}\right)^2 + \left(\frac{\psi'}{2}\right)^2 = \frac{1}{4} \left[ \left( \sqrt[3]{\frac{2a^2V}{c}} \right)^2 + \left( \sqrt[3]{\frac{2V}{ac}} \right)^2 \right].$$

In the last expression the value in (3) is substituted for  $\psi'$ ; the whole expression then further simplifies to :

$$\chi^2 = \frac{1}{4}(1+a^2) \left( \sqrt[3]{\frac{2V}{ac}} \right)^2,$$

from which we finally get :

$$\chi = \frac{1}{2} \cdot \sqrt{1+a^2} \cdot \sqrt[3]{\frac{2V}{ac}}.$$

We have thus independently proved these three formulæ for  $\chi$ ,  $\psi$ , and  $\omega$  directly from first principles.

If it should be desired to compare a pseudo-hexagonal crystal with a truly hexagonal one or a trigonal one of hexagonal habit, care must be taken in calculating the topic parameters that they are strictly comparable with the pseudo-hexagonal ones. Such has been done by Gossner<sup>1</sup> in the case of the double sulphate and double chromate of potassium and sodium,  $K_3Na(SO_4)_2$  and  $K_3Na(CrO_4)_2$ , which are trigonal-hexagonal, yet so similar to potassium sulphate and potassium chromate, considered as pseudo-hexagonal, that Gossner has compared their molecular distance ratios. Their Bravais-Miller axial ratios as trigonal crystals are respectively  $a:c=1:1.2904$  and  $a:c=1:1.2857$ ; but for the purposes of comparison with the pseudo-hexagonal sulphate and chromate, which are rhombic but of pseudo-hexagonal habit, the trigonal axial ratios were converted to rhombic ones, that is, the value of what would be the  $b$  axis on a rhombic assumption was found and the values of  $a$  and  $c$  referred to it as unity. The new values of  $a$  and  $c$  are, of course, such that  $c/a=1.2904$  and  $1.2857$  for the double sulphate and double chromate respectively. In the result, Gossner found that,—while on the one hand the simple sulphate and chromate afforded molecular distance ratios extremely close in value, and on the other hand the two double salts also showed topic axial ratios very near to each other,—yet there was considerable difference between the absolute values for the two pairs of salts, indicating that while the space-lattices were similar their dimensions in space were considerably different. This is just what we should expect, for the two series are not isomorphous in the author's strict "eutropic" sense of the word (see page 383), and the structures are not such as can be so intimately blended as to produce mixed crystals, as is the case with the two members of either pair, which are thus strictly related. This example is given as an indication of the care that must be taken, in making such comparisons, that the constants and formulæ used are themselves strictly comparable; for otherwise such important conclusions can have no value whatever.

The above simple case of pseudo-hexagonal structure, in which we have a rhombic crystal of nearly  $60^\circ$ -prism angle, may have its monoclinic or even triclinic analogue. For deformation may not only occur as to the prism angle, out of  $60^\circ$ , but also the basal plane may be deformed out of the perpendicular to the prism zone, in which case the monoclinic angle  $\beta$  comes into consideration; also the deformation of the prism zone itself from  $60^\circ$  may occur asymmetrically. In both cases the volume is half that of the original monoclinic or triclinic solid the edges of which are parallel to the crystallographic axes. Each case of the kind can be worked out from first principles, from the specific conditions presented, on the lines which have been amply illustrated in this chapter.

One excellent example, which it may be useful briefly to consider, of a monoclinic pseudo-hexagonal crystal, is afforded by the monoclinic form of dimorphous ammonium selenate,  $(NH_4)_2SeO_4$ . This is the form of the salt which is commonly obtained, by crystallising a solution of selenic acid which has been saturated with ammonia gas. The rhombic form isomorphous with the other alkali selenates and sulphates is only known in mixed crystals with one or other of the latter, rubidium selenate mixing the most readily to form perfect transparent crystals, owing to its similar molecular volume and molecular distance ratios; large transparent rhombic crystals of mixed ammonium and rubidium selenates have been found to contain over 60 per cent. of ammonium selenate. It is further remarkable that the monoclinic form of this latter salt retains the pseudo-hexagonal character of the prism zone, so very characteristic of

<sup>1</sup> *Zeitschr. für Kryst.*, 1904, 39, 166.

the rhombic salts of the series. The angle  $ap = (100) : (110)$  is  $59^\circ 38'$ ,  $ap' = (100) : (310)$  is  $29^\circ 38'$ , and  $p'p = (310) : (110)$  is exactly  $30^\circ 0'$ . A typical crystal of ammonium selenate and its stereographic projection have already been illustrated in Figs. 423 (p. 514) and 42 (p. 86), and a reference to these figures will render the positions of the

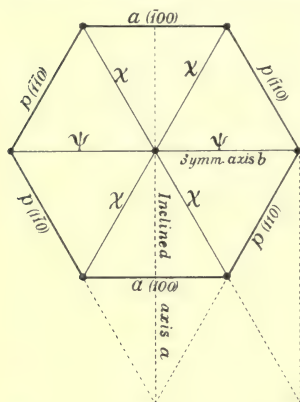


FIG. 474.—Pseudo-hexagonal Space-lattice of Ammonium Selenate.

various faces quite clear. The primary prism  $\{110\}$  of the rhombic crystals appears to correspond, however, to the tertiary prism  $\{310\}$  of the monoclinic crystals, and in the latter, of course, the basal plane is tilted instead of being perpendicular to the prism zone. Fig. 474, reproduced from the author's paper on ammonium selenate,<sup>1</sup> represents a section through the crystal perpendicular to the prism zone  $[apb]$ ; the plane of the paper is no longer parallel to the basal plane, as in Fig. 473, that is, the inclined axis  $a$  lies out of the plane of the paper, except where it intersects the latter at the centre, but the vertical axis is perpendicular to the plane of the paper and the symmetry axis  $b$  lies in the plane. The molecular distance  $\psi$  represents the separation of the structural points along the symmetry axis  $b$ , and  $\omega$  that along the vertical axis;  $\chi$  represents the separation along two equal pseudo-hexagonal axes, inclined

to the plane of the paper, and the plans of which lie at nearly  $60^\circ$  to each other and to the symmetry axis  $b$ . The formulæ employed by the author in calculating the molecular distance ratios were as under :

$$\chi = \frac{1}{2} \cdot \sqrt{1 + a^2} \cdot \sqrt[3]{\frac{2V}{ac \sin \beta}}, \quad \psi = \sqrt[3]{\frac{2V}{ac \sin \beta}}, \quad \omega = \sqrt[3]{\frac{2c^2 V}{a \sin \beta}}.$$

It will be observed that the formulæ for  $\chi$  and  $\omega$  for the monoclinic crystals of ammonium selenate only differ from the corresponding formulæ for the rhombic salts, as given on page 596, by having  $\sin \beta$ , the monoclinic angle between the vertical and inclined axes  $c$  and  $a$ , introduced in the denominator of the fraction. An additional  $\sin \beta$  also occurs in the expression for  $\psi$ , but here, as the axis  $a$  of the rhombic salts corresponds to the symmetry axis  $b$  of the monoclinic salts, the expression contains the term  $\frac{2V}{ac}$  instead of  $\frac{2a^2V}{c}$ ; the expression for  $\psi$ , in fact, is that of  $\psi$  for the rhombic space-lattice as given on page 594, with the addition of  $\sin \beta$  in the denominator.

There still remain to be dealt with those five of the fourteen space-lattices in which points occur either in the centre of the parallelepipedon (Nos. 2, 5, 9, and 11) or in the centre of each of its faces (No. 3).

In the case of space-lattice No. 9 (Fig. 464), in which a point occurs in the centre of a rhombic prism (a prism having a rhombus for base, normal to the vertical axis), if we consider, as usual, each point as representing a molecule, the solid corresponding is a hexaparallelohedron, a combination of the three rhombic prisms  $\{110\}$ ,  $\{011\}$ , and  $\{101\}$ . The volume is one-half of that of the parallelepipedon with rhombic base, that of space-lattice No. 8 (Fig. 463), and with this knowledge and that already acquired as to space-lattice No. 8 the molecular distance ratios, including those involving the central point, can be readily calculated from first principles on the lines already now so fully exemplified in previous pages.

The case of the rectangular rhombic prism with a point at its centre, space-lattice No. 11 (Fig. 466), is similar. The presence of a point at the centre of a

<sup>1</sup> Journ. Chem. Soc. Trans., 1906, 89, 1070.



parallelepipedon having three pairs of unequal but mutually rectangular faces, parallel to the axial planes, renders the solid corresponding to each molecular point a heptaparallelohedron, the combination of a rhombic bipyramid with the three axial-plane pinakoids. The volume is one-half of that of the parent parallelepipedon of Fig. 465, the number of points in the same space being doubled by the introduction of the central points into the space-lattice.

With these data it is easy to work out the molecular distance ratios whenever required, from first principles.

The next is the case of the **tetragonal space-lattice No. 5** (Fig. 456), in which a point is situated in the centre of the tetragonal prism. This introduction of a central point doubles the number of points in the same space and halves the volume, the resulting solid corresponding to each molecular point being a hexaparallelohedron, a combination of the tetragonal prism with the bipyramid. This information is again adequate to enable the molecular distance ratios to be readily calculated.

If the original parallelepipedon be a cube, and a central point is introduced so as to convert it into **space-lattice No. 2** (Fig. 453), the solid corresponding to each molecular point is a heptaparallelohedron, a combination of the cube and octahedron, and the greatest reticular density has been shown to occur along the planes of the rhombic dodecahedron. The volume is one-half of that of the original cube, and with this knowledge the calculation of the molecular distance ratios is a very simple matter.

In the last case of a cube with a point in the centre of each face, **space-lattice No. 3** (Fig. 454), each point corresponds to a solid having the shape of the rhombic dodecahedron, a hexaparallelohedron, and the planes of maximum density have been shown to be those of the octahedron. The volume in this case is one-fourth of that of the original cube, and this fact enables the molecular distance ratios to be calculated without difficulty.

Having now dealt fully with the 14 space-lattices, the fundamental groundwork of crystal structure, a few general observations concerning the 230 types of crystal structure will lead up to an attempt, which will next be made, to render clear the nature of the 65 regular point-systems of Sohncke, and also to show in what manner they are related to the 14 space-lattices. It will subsequently be shown how the remaining 165 types of homogeneous structure are derived from the 65 Sohncke systems, and a tabular presentment of the general relationship will be given.

**The 230 Types of Homogeneous Structures possible to Crystals.**—The advent of the new method of crystallographic investigation by X-rays to be described in Chapter XXXIII. renders still more important the geometrical theory of crystal structure discussed in Chapter XXX., and its 230 methods of arrangement of points, and it is most important for workers in this field of research to have before them a clear presentment of these types which the geometricians have shown to be alone possible to crystal structures. The types are only in the simpler cases hard-and-fast stereotypes, so that within the limits of the great majority of them considerable variety of the details of arrangement are possible, details which it should be the province of investigation by X-rays to reveal. At first sight a difficulty appears to arise in that the structure theory only takes cognisance of points, which are by definition similar, and therefore, if taken to represent atoms, correspond to and represent only one and the same kind of chemical atom; whereas in chemical crystallised substances we are dealing with molecules composed

of a number of atoms of different chemical elements, except in the relatively few cases in which we are dealing with the free elements themselves. This, however, is not a real difficulty, as the atoms of each species (element) take up an arrangement of their own, which can never be of lower, and may even be of higher, symmetry than that of the crystal. The introduction of another kind of elementary atom can never originate symmetry elements which were not already present, but can only more or less impair or destroy those previously there. Von Groth's version of Sohncke's perfected generalisation, given on page 572, shows, in fact, how the interpenetration of the several point-systems, each formed by the atoms of the same chemical element, succeeds in building up the whole combined system, to form the grosser (molecular or polymolecular) structural unit.

Now there can be no doubt that the 65 regular point-systems of Sohncke are fundamental, as they involve only cover-operations (Deckoperationen), or as they are usually termed "coincidence movements," of the first, simpler, kind, namely simple rotations and translations; and also because it is easy to derive the other 165 types of homogeneous structure from them, by adding the operations of the second, more complicated, kind to them, namely, those involving the symmetry centre, the mirror-reflection plane, the gliding-mirror-reflection plane, and the mirror axis. It has been pointed out by W. Voigt,<sup>1</sup> that this method of derivation, beginning with the Sohncke 65 systems and thence deriving, by adding the second kind of operations, the other 165 systems, is probably both the most satisfactory, as well as the simplest method of procedure. It is practically that followed by Fedorov and by Barlow, and although Schönflies proceeded from first principles in a more general manner, and by his method derived the 65 Sohncke systems as they came along, interspersed with the more complicated ones, it is easy to collate the Schönflies systems into groups, as derived from and corresponding to each of the 65 fundamental Sohncke systems. This method will therefore be adopted here.

It should be made clear that the same principles, based on operations or coincidence movements of the first and second kinds, govern the symmetry both of the crystals themselves, that is, that of the 32 classes, and the symmetry of the groups of movements which lead to the 230 types of homogeneous structure. Both are limited, the first obviously and the second because only such types are admitted among the 230 as are possible to crystals, by the law of rational indices. But the two applications are distinguished by the fact that in the case of the 32 crystal classes all the axes pass through the same point, the common centre of the crystal and of the sphere with which we imagine it to be enveloped for the purposes of the stereographic projection of its symmetry. That is, the coincidence movements are finite in character, although they can be imagined as being moved parallel to themselves anywhere within the crystal. On the other hand, the rotation axes, screw axes, and other movements, are infinitely many in the case of the geometrical theory of homogeneous structures; for the structure is unlimited, similar atoms being repeated indefinitely on every hand throughout the structure or

<sup>1</sup> *Phys. Zeitschr.*, 1918, 19, 237 and 446.



assemblage, which is assumed to be extended without limit. Instead of a single axis in any particular direction there are now groups or bundles of axes. In all cases, however, when several axes pass through the same point, and thus mutually intersect, the ordinary crystallographic laws apply.

The crystal system is in general determined by the coincidence movements (Deckoperationen) of the first kind possessed by the crystal, and not by those of the second kind, which have to do with the crystal class, which latter, if any such second-kind movements are operative, they decide. Operations of the first kind may be described as essentially simple rotations about axes (which in the case of crystal symmetry pass through the centre of the sphere of the spherical and stereographic projection), and simple translations. Operations of the second kind are rotations combined with inversion to the other side of the centre; in the cases of homogeneous structures (the 230) possible to crystals, these second-kind operations are of four sorts, involving (1) the symmetry centre; (2) the mirror-reflection-plane; (3) the latter combined with a gliding along the plane; and (4) the mirror axis.

It will be shown in the chapter (XXXIII.) on X-rays and Crystals that most<sup>1</sup> of the substances the structures of which have so far been elucidated by means of X-rays prove to involve no coincidence movements of the second kind at all, and that they either at once correspond to simple space-lattices, or to one of the 65 Sohncke regular point-systems, or else to one or other of the special cases of such which have been described by Sohncke in describing his extended method. Hence, it is indubitably true that these 65 regular point-systems are indeed fundamental, and it is clearly, therefore, essential that they shall next be described.

**The 65 Regular Point-systems of Sohncke.**—Having already in pages 582-588 fully described the 14 Frankenheim-Bravais space-lattices, it is not only necessary from the above point of view, but will doubtless also be a convenience to workers in the new domain of investigation of crystal structure by means of X-rays, that some account with illustrative figures should be given of the 65 regular point-systems of Sohncke. For these are the simpler of the whole 230 arrangements of points corresponding to the types of homogeneous structures possible to crystals. They are, namely, as already stated, those involving operations, coincidence movements (Deckoperationen), which are of the "first kind" only. An operation of the first kind is of the nature of a rotation, which may not merely be, however, simple rotation about a  $n$ -fold axis, but may in the case of these unlimited assemblages of points possibly be (and frequently is) a spiral rotation about a screw-axis. That is, any one of Sohncke's point-systems is brought to coincidence with itself by rotation or rotations

<sup>1</sup> Of all the substances referred to in that chapter as having been dealt with by W. Voigt in his memoir already referred to, *Phys. Zeitschr.*, 1918, 19, 446, only three, iron pyrites  $\text{FeS}_2$  and its analogues hauerite  $\text{MnS}_2$  and cobalt-glance  $\text{CoSAs}$ , are sufficiently complicated to require second-kind coincidence movements for their elucidation. All the others are immediately referable to specific Sohncke regular point-systems or their specialised forms in which only first kind operations are involved.



about an axis or axes, which in many cases are not simple rotation-axes but screw-axes, the movement necessary to effect coincidence again being of the character of a screw thread. This will be more clearly realised as the point-systems are described.

A movement or operation of the "second sort" does not, like one of the first sort, bring the body to identity or coincidence with itself, but into the mirror-image body. That is, the coincidence movement of the second kind is of the nature of a reflection at a plane. The simplest operation of the second sort is, indeed, simple mirror-image reflection itself, each point and straight line passing over into its mirror-image. A rotation may, however, also occur, and if its axis be perpendicular to the plane of reflection and the angle of rotation be  $180^\circ$  we have the particular kind of second-sort operation known as "inversion." Inversion replaces every point by a point diametrically opposite, on the other side of the origin. The more general form of a second-sort operation, however, is not so restricted, but consists of the mirroring movement about a plane and a rotatory movement, not necessarily for  $180^\circ$ , about a fixed point in the plane—what is known as a rotatory reflection—the axis of rotation passing through the fixed point. Mirror-image reflection purely and simply, and inversion, are the two special cases of this general case, when the angles of rotation are respectively  $0^\circ$  or  $180^\circ$ .

Thus the typical movement of the first kind is rotation about an axis, and every movement about a fixed point is equal to such a rotation. The typical movement of the second kind is rotatory reflection, the combination of a reflection and a rotation, the axis of the latter being perpendicular to the plane of the former.

The two special cases which have been mentioned, mirroring and inversion, are, however, of such immense importance that they suffice for the derivation of nearly all the remaining 165 cases of the 230, the general case of rotatory reflection being only required for the elucidation of a very few types of more complicated homogeneous structure.

It was by the use of second-kind operations or coincidence movements, as well as of first-kind movements, that Schönflies was enabled to deduce the whole 230 types of structure possible to crystals. Barlow, in his independent labours to the same end, started first with the 65 first-kind point-systems of Sohncke, and then derived from them 92 other types by multiplying by an inversion, that is, by performing inversion with them. Then he proceeded further to derive from them 71 more types by use of the second-kind movement which we term reflection (the movement is in these cases, however, more accurately described as isomorphous with a reflection, as translation also occurs). And lastly he derived the two remaining types by employing the general movement of the second kind, that of rotatory or screw reflection. It is, indeed, remarkable that Barlow should have been able to derive all but two of the 230 types of homogeneous structure without having recourse to the most general of all possible cases of second-kind coincidence movements.

From the above it will be apparent how very important are the 65 regular point-systems of Sohncke; they may well be considered as the

first superstructure after the 14 space-lattices. A reproduction is given, therefore, of Sohncke's original drawings, together with the necessary short description of each system, following Sohncke's own words as far as clarity of translation from his German text permits, and a list is appended showing their distribution among the 32 classes of crystals.

In his original work *Entwicklung einer Theorie der Krystallstruktur* (Leipzig, 1879) Sohncke describes 66 regular point-systems. In a subsequent memoir,<sup>1</sup> however, he points out that point-systems Nos. 9 and 13 are identical, reducing the total to 65. In the still later memoir<sup>2</sup> in which he indicates the distribution of the 65 systems among the 32 crystal classes, he retains the original numbering of the point-systems up to 66, and simply omits No. 13. It has been thought best in this book to re-number the point-systems from Sohncke's No. 14 to his No. 66, so as to make them read in proper sequence 13 to 65. Hence the author's numbers here given from 13 to 65 will correspond to the systems to which Sohncke attaches the numbers one unit greater in each case; thus, say for instance, the author's No. 21 will correspond to Sohncke's No. 22. Since the author wrote this chapter a description of Sohncke's point-systems has also been given by W. Voigt,<sup>3</sup> who has also happily adopted the same course. The eliminated No. 13 is shown in Fig. 474a; it was termed by Sohncke "The System of the Rhombic Prism of the Second Kind."

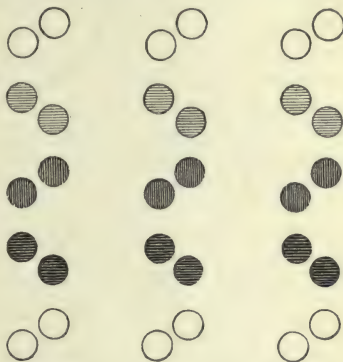


FIG. 474a.—Sohncke's original (now eliminated) No. 13 Point-system.

With regard to the relationship between Bravais space-lattices and Sohncke point-systems, Sohncke states that every regular and unlimitedly extended point-system consists in general of several interpenetrating congruent space-lattices; in certain special cases, however, the point-system becomes reduced directly to a single space-lattice. This will be clearly pointed out in describing the particular point-systems in question, after the description of the general form. The coincidence movements of the system are identical in all cases with those of the fundamental space-lattice (page 178 of Sohncke's book). Sohncke also points out that the points of the Bravais space-lattice represent molecules (or, as we now more accurately know, in many cases a small group of molecules), and that these in turn are composed of atoms, which may be arranged as the points of a Sohncke system; for it is generally possible to find groups of the points such that the centres of gravity of these groups are arranged in a space-lattice. To this must be added, in the light of the work of Schönflies, Fedorov, and Barlow, that the atoms composing the molecule or small group of molecules (the centres of gravity or other analogous

<sup>1</sup> *Zeitschr. für Kryst.*, 1886, 14, 423.

<sup>2</sup> *Ibid.*, 1892, 20, 445.

<sup>3</sup> *Phys. Zeitschr.*, 1918, 19, 447.

representative points of which molecules or groups form the space-lattice) may also be arranged according to one of the other 165 systems of points, involving operations of the second kind; that is, the system may not be simply that of one of the 65 types of Sohncke involving operations only of the first kind, but may rather be that of one of the combinations of those 65 systems, involving the second kind of coincidence movements.

In the figures illustrating the 65 systems in the following description, the axes of the coincidence movements to which the points are subject are omitted for the sake of clearness. Each point of the system is represented by a little circle, which is unshaded if it be supposed to lie in the plane of the figure, and is shaded the more deeply according to the distance which is supposed to separate it from the plane of the paper. The successive  $n$ -points of a  $n$ -point screw thus appear as  $n$  little circles, of which every successive one is shaded more deeply than the preceding one, and the centres of which are arranged in a circle. The screw is supposed to be right-handed or left-handed according as one considers the increasing depth of shading to mean further and further removal **below** or **above** the plane of the figure. With the exception of Nos. 1, 53, and 58, each little circle is supposed to be the projection of an infinite number of points, arranged over one another at equal distances apart. The overlapping pairs of circles—of which one circle is drawn completely, but the other is only partly visible—are intended to represent two points lying very close together at different distances from the plane of the figure, just as if they were two balls, one of which is partly behind and consequently partially hidden by the other. The fact that the points are represented by circles must not be taken to mean that they stand for spherical atoms; the shape or form of atoms is not intended to be implied in any way. The figures for Nos. 56, 57, 61 to 65 consist of three portions separated by rectangularly crossed lines. Each of these systems consists of three part-systems inserted through each other in three perpendicular directions. For greater clearness each part-system is separately projected on one of the three principal planes perpendicular to the principal axes of the three part-systems.

**No. 1. The Space-lattice without Rotation Axes.**—Regular infinite point-systems without axes of rotation or screw-axes are space-lattices with parallelepipedal meshes. They are formed by the intersection points of three trains of parallel equidistant planes. This regular point-system No. 1 is represented in Fig. 475, and is identical

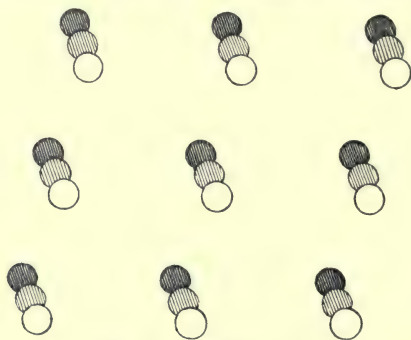


FIG. 475.—Sohncke's No. 1.

with the Bravais triclinic space-lattice No. 14, as described on page 588 and illustrated in Figs. 447 and 469.

**No. 2. The Two-fold Prism System.**—This consists of points which bestrew the limiting lines of parallel congruent strips, or, in other words, the edges of two-fold



columns, at equal distances and at equal heights above a single principal plane. The middle lines of these strips are formed by one kind of axis. All principal planes are bestrewn with pairs of points and the figure (Fig. 476) shows such a principal plane.

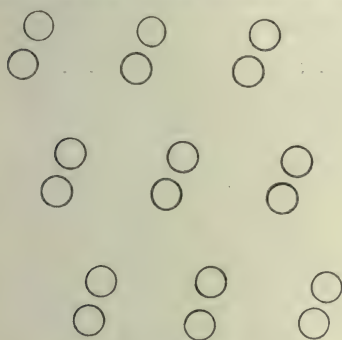


FIG. 476.—Sohncke's No. 2.

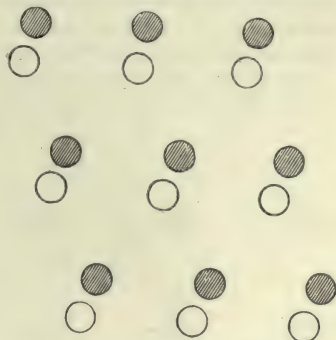


FIG. 477.—Sohncke's No. 3.

**No. 3. The Two-point Screw System.**—This consists of parallel congruent two-point screws, which are brought into coincidence by translation perpendicular to the axis, and the axes of which form in the principal plane a parallelogram-meshed net. All principal planes are bestrewn with congruent parallelogrammic point-lattices. It is shown in Fig. 477.

**No. 4. The Clinorhombic Prism System.**—This system, shown in Fig. 478, may be termed also the system of the two-fold octahedron. It may be regarded as consisting of two parallel interpenetrating congruent columnar systems, of which one is raised above the other by a half-column height. Two adjacent principal planes give together the same projection figure as the whole system, whilst the alternate rows of point-pairs belong to either one or the other principal plane. The centres of all the point-pairs form a clinorhombic space-lattice, No. 12 (Fig. 467, page 587), the axis of the clinorhombic (monoclinic) prism running right and left in Fig. 478.

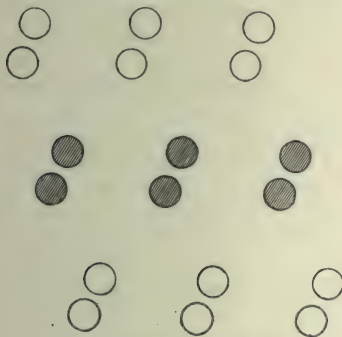


FIG. 478.—Sohncke's No. 4.

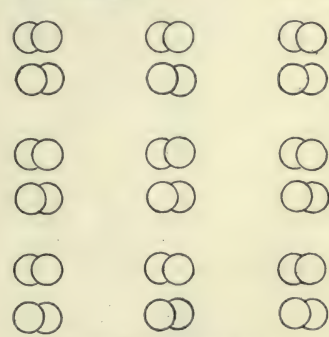


FIG. 479.—Sohncke's No. 5.

There are two interesting special cases of this system: (a) When the elementary parallelogram is rectangular, and both rotation axes pass through neighbouring corners, the middle points of the point-pairs form the orthorhombic prismatic space-lattice No. 8 (Fig. 463, page 586). (b) When the parallelogram is rectangular but the rotation axes are diagonally arranged, the middle points of the point-pairs form a rhombic octahedral space-lattice (that of the centred rhombic prism), No. 9 (Fig. 464).

**No. 5. The Rectangular Prism System.**—This, shown in Fig. 479, originates out of the two-fold prism system No. 2. All the two point-pairs, belonging to one and the other part-system, stand closely over each other, and form an equifaced tetrahedron, which projects into a right angle of the figure. The whole system consists of such congruent parallel tetrahedra, the centres of which form a rectangular parallelepipedal space-lattice, No. 10 (Fig. 465, page 586).

**No. 6. The Compound Rectangular Two-point Screw System.**—This is shown in Fig. 480. It originates out of the two-point screw system No. 3, and consists of

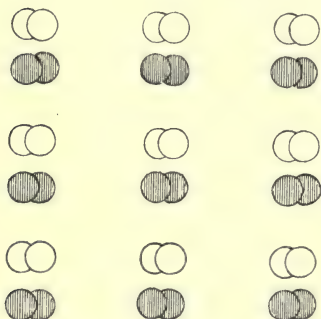


FIG. 480.—Sohncke's No. 6.

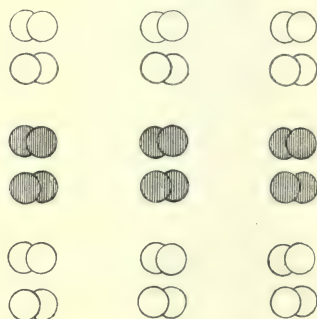


FIG. 481.—Sohncke's No. 7.

compounded two-point screws, the axes of which fall together with one of the kinds of two-fold rotation axes, and thus produce a rectangular net. The point-pairs replace the single points of the simple screw system.

**No. 7. The Rhombic Prism System.**—This originates out of the special case already referred to of the clinorhombic prism, No. 4, when the middle points of the point-pairs form the orthorhombic prism. It is represented in Fig. 481. By doubling the system two point-pairs are present instead of every single point-pair, and form a regular tetrahedron. The system thus consists of parallel congruent equifaced tetrahedra, the centres of which form the space-lattice of the orthorhombic prism No. 8 (Fig. 463).

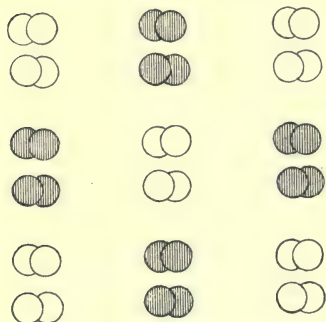


FIG. 482.—Sohncke's No. 8.

**No. 8. The Rhombic Octahedron System.**—This originates out of the second special case of system No. 4, two point-pairs again replacing each point-pair, and together forming a regular tetrahedron. The system, shown in Fig. 482, therefore consists of congruent parallel equifaced tetrahedra, the centres of which form the space-lattice of the centred rhombic prism No. 9 (Fig. 464 on page 586). It may be regarded as formed out of two congruent systems of the kind previously described, which are inserted inside one another parallelwise, so that the centres of the tetrahedra of the one part-system fall in the middle of the rhombic prismatic meshes formed by the centres of the

other part-system. The centres of six neighbouring tetrahedra form the corners of a rhombic octahedron.

**No. 9. The Compound Rhombic Two-point Screw System.**—This originates out

of the two-point screw system No. 3. It consists, as shown in Fig. 483, of compounded two-point screws, the axes of which fall in with the one kind of two-fold axis, and thus form a rhombic net. The construction axis halves the separation of a point-pair while the latter replaces the single points of the simple originating system.

**No. 10. The Oblong Octahedron System.**—This originates out of a third special case of the clinorhombic prism system, No. 4, by rotation about a rectangular axis

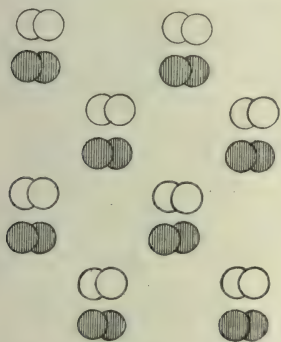


FIG. 483.—Sohncke's No. 9.

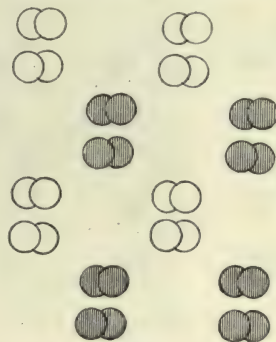


FIG. 484.—Sohncke's No. 10.

which intersects two neighbouring rotation axes. At the same time for every point-pair two pairs of points are introduced, which form the corners of an equifaced tetrahedron. The system thus consists, as indicated in Fig. 484, of congruent parallel equifaced tetrahedra, which are so arranged as if there were two congruent systems of the rectangular prism inserted parallelwise within one another, so that the centres of the tetrahedra of the one system fall in the middle of the rectangular parallelepipedal meshes of the other. The centres of six adjacent tetrahedra thereby form the corners of an oblong octahedron, space-lattice No. 11 (Fig. 466).

**No. 11. The Rhombic Counter-screw System.**—This originates also out of the same third special case of the system of the clinorhombic prism No. 4 which has just been referred to under No. 10, by rotation also about a rectangular axis, but which intersects two other adjacent axes than those intersected in No. 10, causing again two new point-pairs to project symmetrically between the former ones, but in this case inversely arranged to the arrangement in No. 10. The system, shown in Fig. 485, may be considered as two compounded rectangular two-point screw systems, which are inserted so within one another that the axes of the screws of one part-system run in the middle lines of those rectangular prisms which are formed by the screw-axes of the other part-system, but so that the one part-system is translated half the prism-height along the principal axis. Four succeeding points of a cylinder-mantle about one axis form a kind of irregular four-point screw, which is repeated about the adjacent axis, but with the thread wound in the opposite (complementary) direction. A special case occurs when each equifaced tetrahedron concentrates on its centre of gravity, when these centres of gravity form a centred rectangular parallelepipedal space-lattice, that of the oblong octahedron (No. 11, Fig. 466).

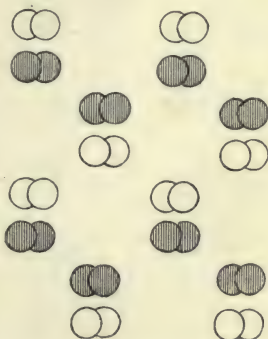


FIG. 485.—Sohncke's No. 11.



**No. 12. The Alternating Rectangular Two-point Screw System of the First Kind.**—In this system, shown in Fig. 486, two groups of two-point screws are so inserted interpenetratingly within one another as to appear as if they were pushed out of the completely mirror-image position by translation along the screw-axis.

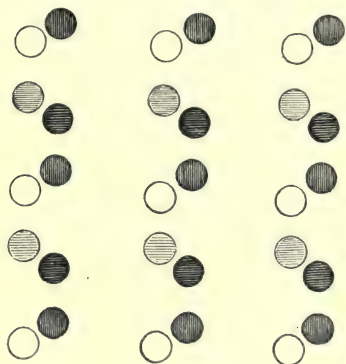


FIG. 486.—Sohncke's No. 12.

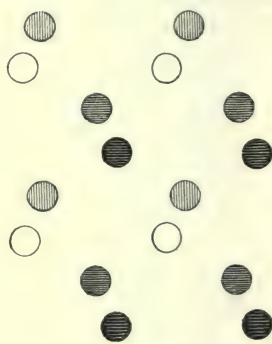


FIG. 487.—Sohncke's No. 13, originally his No. 14.

**No. 13. The Alternating Rectangular Two-point Screw System of the Second Kind.**—Here are two congruent groups of two-point screws opposed to one another, inserted within one another so that the axes of the screws of one group run in the middle lines of those rectangular prisms which are formed by the axes of the screws of the other group. The system is represented in Fig. 487.

**Nos. 14 and 15. The Right and Left Three-point Screw Systems.**—These consist of parallel congruent three-point screws, which can be brought into coincidence by a translation perpendicular to the axis, and the axes of which determine a net of equilateral meshes. All principal planes are bestrewn with congruent point-lattices of equilateral triangular meshes, as shown in Fig. 488.

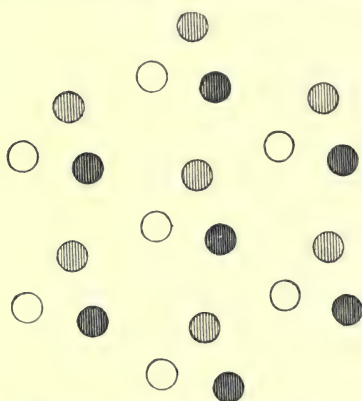


FIG. 488.—Sohncke's Nos. 14 and 15.

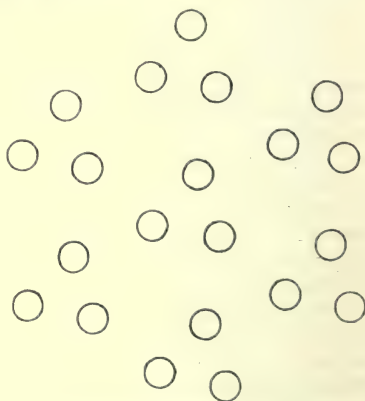


FIG. 489.—Sohncke's No. 16.

**No. 16. The Trigonal Prism System.**—This consists of points which bestrew the edges of parallel congruent prisms standing on equilateral triangular bases, at equal distances and at equal heights above one and the same principal plane. The principal planes are congruently bestrewn, all carrying points arranged in congruent equilateral triangles. Fig. 489 represents such a principal plane.

**No. 17. The Rhombohedron System.**—In this system the points are arranged in three-sided columns like No. 16, that is, in the corners of congruent parallel equilateral triangles. But the latter lie in three successive planes arranged at one-third axial distance, and so that they are laterally displaced in the manner shown in the figure; their centres thus form a rhombohedral space-lattice, No. 7 (Fig. 462 on page 586). Fig. 490 shows three such successive planes of points.

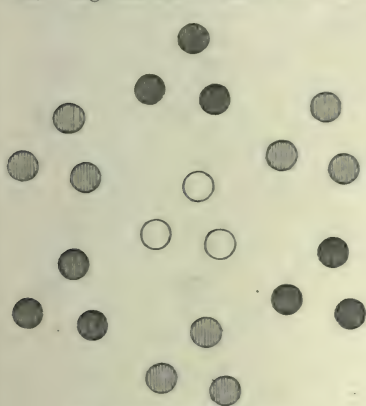


FIG. 490.—Sohncke's No. 17.

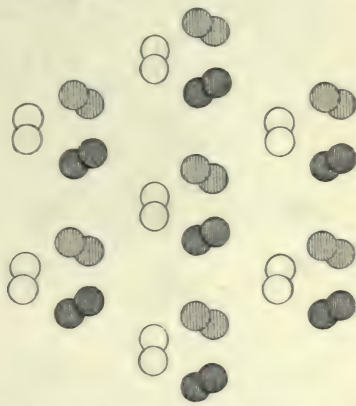


FIG. 491.—Sohncke's Nos. 18 and 19.

**Nos. 18 and 19. The Right and Left Compound Three-point Screw Systems.**—These two complementary systems consist of parallel compound three-point screws, that is, of screws of which each of the three points is double (a point-pair). Each screw consequently projects into a semi-regular hexagon, as indicated in Fig. 491.

**No. 20. The Compound Trigonal Prism System.**—In this system, represented in Fig. 492, every two equilateral triangles belonging to the one and to the other part-system



FIG. 492.—Sohncke's No. 20.

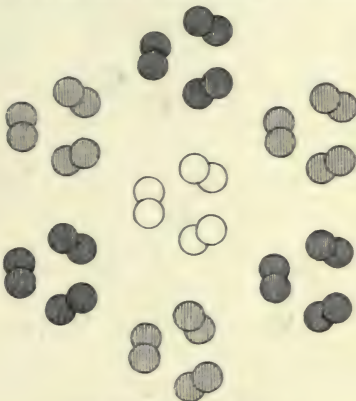


FIG. 493.—Sohncke's No. 21.

respectively stand adjacently over one another, and form a spirally wound three-sided prism, the projection of which on the principal plane is a hexagon. The whole system consists of congruent parallel spirally wound prisms, the centres of which form the space-lattice of the regular three-sided (trigonal) prism No. 6 (Fig. 457 on page 584).

**No. 21. The Compound Rhombohedron System.**—This system, represented in Fig. 493, is distinguished from the simple rhombohedron system only by the fact

that there are wound prisms instead of equilateral triangles. The entire system consists of congruent parallel but spirally wound three-sided prisms, the centres of which form the rhombohedral space-lattice No. 7 (Fig. 462).

**Nos. 22 and 23. The Right and Left Alternating Three-point Screw Systems.**—These complementary systems consist of two interpenetrating simple screw systems, which run in opposite directions. They differ from Nos. 18 and 19 in that the relative positions of the compounded screws are different. Those two previously described systems are reproduced if all the screws are rotated  $30^\circ$  about their axes. Each principal plane is bestrewn with a point-lattice of equilateral triangular meshes, and Fig. 494 is the projection of six such successive principal planes.

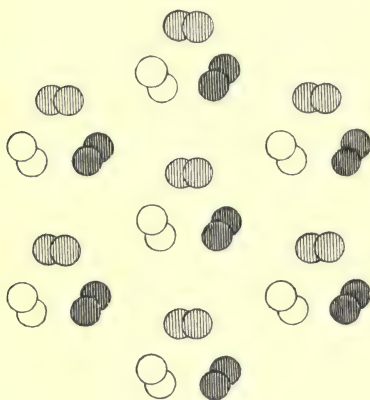


FIG. 494.—Sohncke's Nos. 22 and 23.

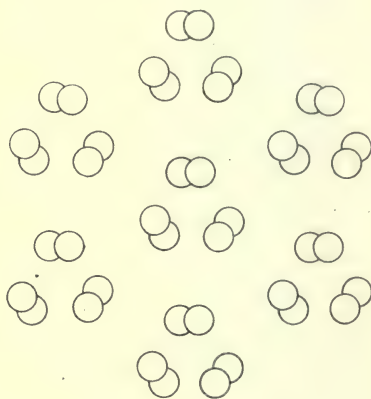


FIG. 495.—Sohncke's No. 24.

**No. 24. The Alternating Trigonal Prism System.**—This consists of two interpenetrating three-sided prism systems, No. 16, and it is distinguished from the compound trigonal prism system No. 20 only by the fact that all the columns are here rotated  $30^\circ$  about their axes, compared with their previous positions. Each principal plane is bestrewn with the corner points of parallel congruent equilateral triangles. Fig. 495 is the projection of two such planes.

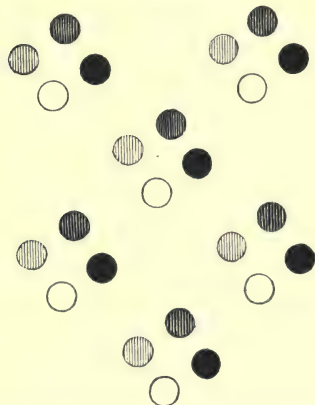


FIG. 496.—Sohncke's Nos. 25 and 26.

**Nos. 25 and 26. The Right and Left Four-point Screw Systems.**—These consist of parallel congruent four-point screws, which are brought into coincidence again by translation perpendicular to the axis. Their axes form in the principal plane a net of tetragonal meshes. All principal planes are bestrewn with congruent point-lattices of tetragonal mesh, as shown in Fig. 496.

**No. 27. The Fourfold Counter-screw System.**—This system, indicated in Fig. 497, may be regarded as formed by two congruent screw systems, which interpenetrate with their axes parallel, and so that the screw-axes of the one run midway between four surrounding adjacent screw-axes of the other, and so also that the one system is raised half a screw turn above the others. The principal



planes are bestrewn congruently, and follow each other at one-fourth the screw-height pitch. Each carries two congruent parallel interpenetrating tetragonal point-lattices, but the bestrewing of each succeeding plane occurs in such a manner that the points are rotated  $90^\circ$  from the positions occupied in the previous plane.

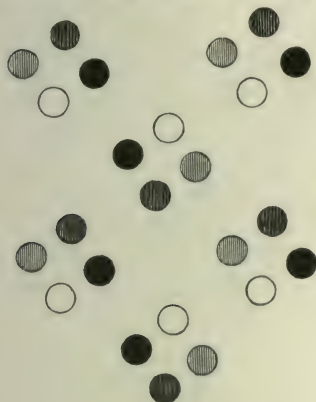


FIG. 497.—Sohncke's No. 27.

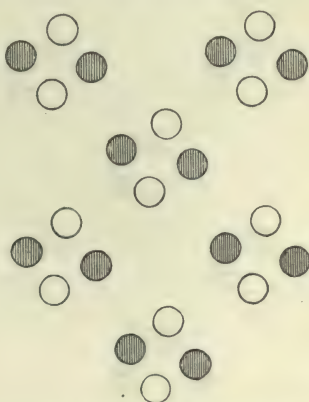


FIG. 498.—Sohncke's No. 28.

**No. 28. The Double-threaded Four-point Screw System.**—This consists of parallel congruent double-threaded screws, each formed of two interwound four-point screws, and which are brought into coincidence by a translation perpendicular to the axis. The principal planes follow at equal half-pitch intervals; alternate planes carry point-pairs which lie as the diagonals, in one direction, of the squares in Fig. 498, and the other alternate ones are similar, but with the point-pairs along the other diagonals.

**No. 29. The Tetragonal Prism System.**—This consists of points bestrewn the edges of parallel congruent square prisms, at equal distances and at the same height above the principal plane. The principal planes are congruently bestrewn with points arranged in congruent squares. Fig. 499 shows such a plane.

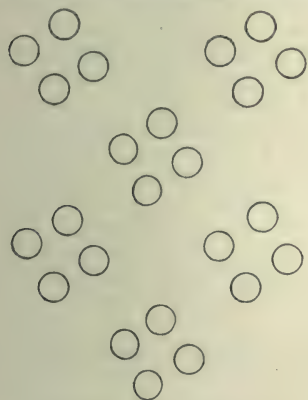


FIG. 499.—Sohncke's No. 29.

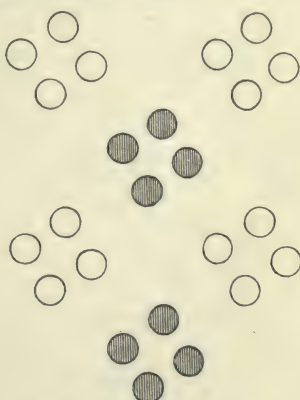


FIG. 500.—Sohncke's No. 30.

**No. 30. The Tetragonal Octahedron System.**—This system, represented in Fig. 500, may be regarded as consisting of two parallel midway interpenetrating congruent

square prism systems, of which one is raised half a prism-height above the other. Two adjacent planes give together the same projection figure as the entire system, while the alternate squares belong respectively to the one and to the other system.

**Nos. 31 and 32. The Right and Left Compound Four-point Screw Systems.**—Each of these consists, as shown in Fig. 501, of parallel congruent compound four-

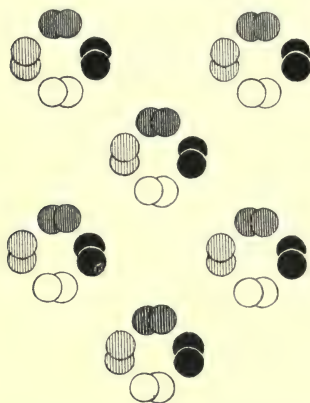


FIG. 501.—Sohncke's Nos. 31 and 32.

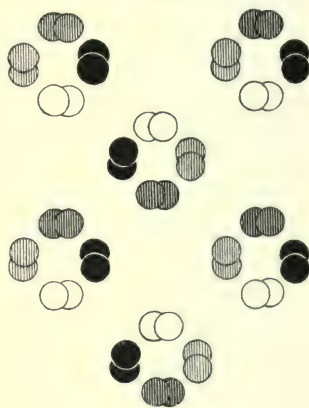


FIG. 502.—Sohncke's No. 33.

point screws, which coincide after a translation perpendicular to the principal axis, and project into a semi-regular octagon.

**No. 33. The Four-fold Compound Counter-screw System.**—This may be regarded as consisting of two congruent compound screw systems, which interpenetrate in such a parallelwise manner that the screw axis of the one runs in the middle between the four similar axes of the other system. The character of the thread of the one

set of four is the opposite of that of the other set of four, as will be clear from Fig. 502. The pitch of all the screws is the same.

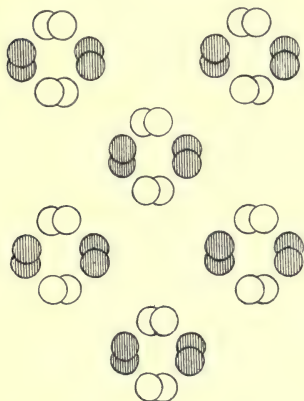


FIG. 503.—Sohncke's No. 34.

**No. 34. The Double-threaded Compound Four-point Screw System.**—This system, shown in Fig. 503, only differs from the corresponding single system No. 28 in having pairs of points instead of single points. Two successive principal planes form a layer of congruent parallel equifaced tetrahedra, the centres of which are arranged as square net meshes, and the rotation axes of which run parallel to the principal axis and to the mesh sides. The next layer is congruent with the previous one, but rotated  $90^\circ$  about the principal axis. Each axis thus carries at equal distances the centres of the tetrahedra, but the latter are only alternately parallel, while the neighbouring ones are crossed.

**No. 35. The Compound Tetragonal Prism System.**—In this system, represented in Fig. 504, the two squares belonging to the two part-systems stand adjacently over one another, and form a spirally wound four-sided column, the projection of which on the principal plane is an octagon. The entire system consists of congruent parallel spirally wound columns, the centres of which form the space-lattice of the tetragonal prism No. 4 (Fig. 455 on page 583).

**No. 36. The Compound Tetragonal Octahedron System.**—This system, shown in Fig. 505, may be regarded as composed of two parallel midway interpenetrating

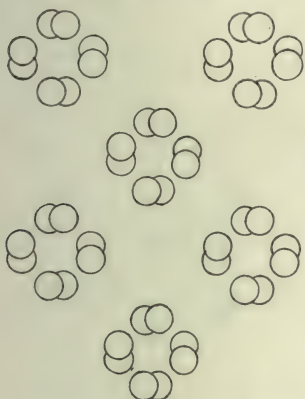


FIG. 504.—Sohncke's No. 35.

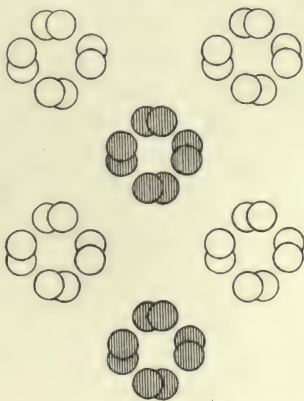


FIG. 505.—Sohncke's No. 36.

congruent systems of the previous No. 35 kind, but of which one is raised above the other a half-column height. Parallel congruent spirally wound prisms stand so side by side that their centres form the tetragonal octahedral space-lattice No. 5 (Fig. 456).

**Nos. 37 and 38. The Right and Left Alternating Four-point Screw Systems.**—These consist of two interpenetrating simple screw systems, so that successive screws belong alternately to the one system and to the other. Every principal plane is in general bestrewn with a tetragonal point-lattice, and Fig. 506 is the projection of eight such successive planes.

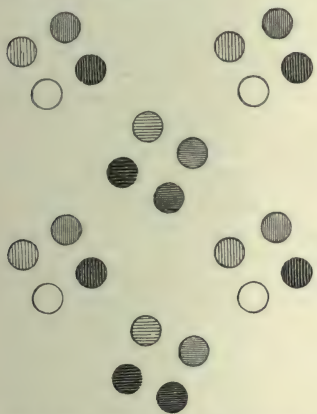


FIG. 506.—Sohncke's Nos. 37 and 38.

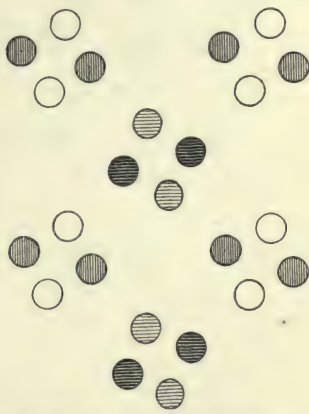


FIG. 507.—Sohncke's No. 39.

**No. 39. The Alternating Double-threaded Four-point Screw System.**—This consists of two interpenetrating double-threaded four-point screw systems, so that each principal plane is bestrewn with pairs of points, which together form two interpenetrating congruent tetragonal point-lattices. Fig. 507 is the projection of four successive principal planes.

**No. 40. The Alternating Tetragonal Prism System.**—This consists of two inter-



penetrating tetragonal column systems. Each principal plane is in general bestrewn with the corner points of congruent parallel squares. Fig. 508 is the projection of two neighbouring principal planes. A special case of interest is that which occurs when the squares reduce themselves to points, which then correspond to two interpenetrating congruent

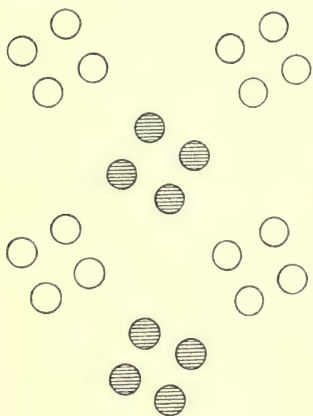


FIG. 508.—Sohncke's No. 40.

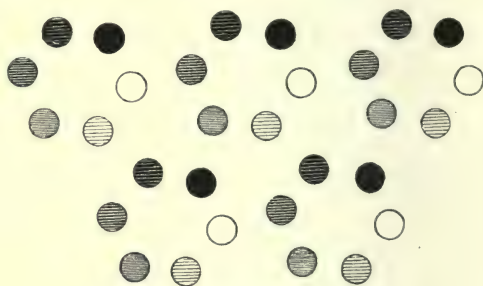


FIG. 509.—Sohncke's Nos. 41 and 42.

space-lattices of the tetragonal prism No. 4 (Fig. 455).

**Nos. 41 and 42. The Right and Left Six-point Screw Systems.**—These consist,

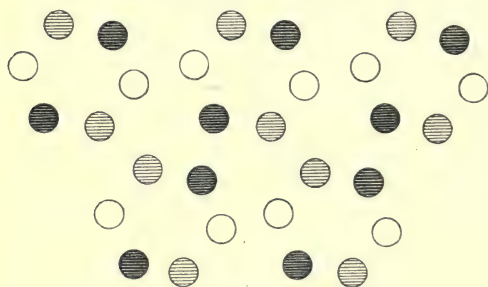


FIG. 510.—Sohncke's Nos. 43 and 44.

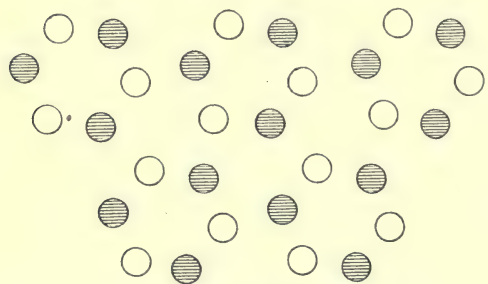


FIG. 511.—Sohncke's No. 45.

as shown in Fig. 509, of parallel congruent six-point screws, which can be brought to coincidence by a translation perpendicular to the axis, and the axes of which form in the principal plane a net of equal-sided three-cornered meshes. All principal planes are bestrewn with congruent point-lattices of equal-sided three-cornered meshes. The two systems are alike except as regards the right- or left-handed character of the winding of the screw thread.

**Nos. 43 and 44. The Right and Left Double-threaded Six-point Screw Systems.**—These consist of two congruent interwound six-point screws, starting from two diametrically opposite points of the screw cylinder, so that midway between every two points (corresponding to the pitch) of one screw there is situated a point

of the other screw. The principal planes are bestrewn congruently, but every successive plane is rotated  $60^\circ$  about a six-fold axis with respect to the preceding one. Fig. 510 represents the case.

**No. 45. The Triple-threaded Six-point Screw System.**—This system, shown in Fig. 511, consists of three congruent interwound six-point screws, starting from three points on the screw cylinder, which form an equilateral triangle lying in a principal plane, and so that the height of the pitch (one turn) on one screw is divided into three parts by the two intermediate points of the two other screws. The principal planes are congruently bestrewn, the points which they alternately carry being arranged in equilateral triangles, arranged congruently and parallelwise; but those of each successive plane are rotated  $60^\circ$  with respect to those of the preceding plane.

**No. 46. The Hexagonal Prism System.**—This consists of points which bestrew the edges of congruent parallel hexagonal prisms, at equal distances and at equal heights. The principal planes are bestrewn with points arranged congruently in regular hexagons. Fig. 512 represents such a principal plane.

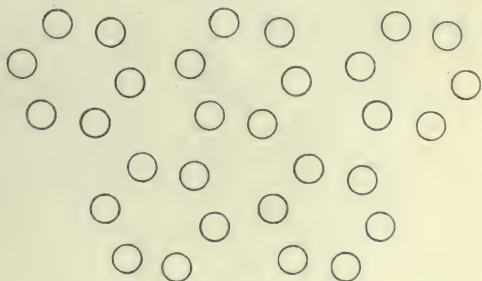


FIG 512.—Sohncke's No. 46.

**Nos. 47 and 48. The Right and Left Compound Six-point Screw Systems.**—These differ from the simple six-point screw systems Nos. 41 and 42 only in the fact that pairs of points are now present instead of single points. The arrangement will be clear from Fig. 513.

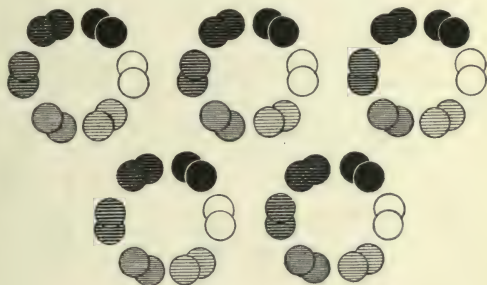


FIG. 513.—Sohncke's Nos. 47 and 48.

**Nos. 49 and 50. The Right and Left Double-threaded Compound Six-point Screw Systems.**—In the systems 43 and 44 two points lie at the ends of a diameter of the screw cylinder. The two systems now under consideration are formed if this single diameter be replaced by two closely adjacent diameters with points at their ends. The four points together form an equifaced tetrahedron, and the whole system consists of layers of such congruent parallel tetrahedra, the centres of which form a net of equilateral triangular meshes. Three such layers are shown in Fig. 514, and afford the same projection as the whole system.

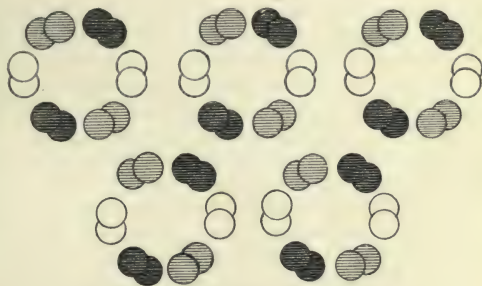


FIG. 514.—Sohncke's Nos. 49 and 50.

**No. 51. The Triple-threaded Compound Six-point Screw System.**—In this system,

shown in Fig. 515, two triangles belonging to the two part-systems stand closely over one another, and their corners form a three-sided screw column. Every principal axis is bestrewn with such spirally wound columns, which are alternately rotated  $60^\circ$

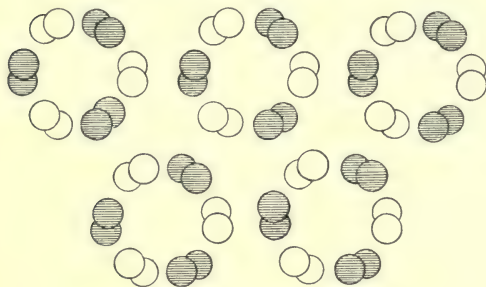


FIG. 515.—Sohncke's No. 51.

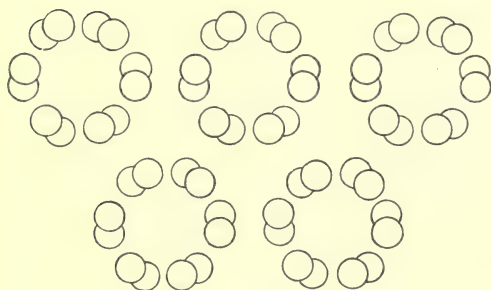


FIG. 516.—Sohncke's No. 52.

they may have either their corners or their sides turned towards each other. The hexagons may also be further contracted until they concentrate on their centres; the central points thus formed produce the trigonal space-lattice (that of the three-sided prism) No. 6 (Fig. 457 on page 584). Also the 12-pointer ring may become a regular 12-sided polygon, lying entirely in the principal plane, and this special case of system 52 is distinguished by its very high symmetry.

**No. 53. The Cubic Twelve-pointer System.**—This originates out of the system of the rectangular prism No. 5, by making the three sets of edges of the rectangular parallelepipedal axial space-net all equal to one another. The parallelepipeda, now cubes, are brought into coincidence by rotation about the cube diagonals, acting as three-fold axes. Thus three rectangular prism systems (in which the centres of the equifaced tetrahedra form a cubic net) interpenetrate in three perpendicular directions (the cube edges), so that three prism axes always stand perpendicular to one another at a common point. This point is the common centre of three equifaced tetrahedra, which are inserted through one another in three perpendicular directions. Their twelve-corner points form the 12-pointer, and Fig. 517 shows one projected on a plane formed by two two-fold axes. The system consists of congruent parallel 12-pointers, the centres of which form a cubic space-lattice, No. 1 (Fig. 452 on page 583).

round the axis with respect to each other. Every twelve-point ring in the figure is the projection of two (and similarly *ad infinitum*) spirally wound columns arranged around the same axis.

**No. 52. The Compound Hexagonal Prism System.**—In this system there are always two hexagons belonging to the one and to the other part-system, closely adjacent over one another. Their corners form a spirally wound hexagonal column. Each twelve-point ring in Fig. 516 is the projection of one such column. The figure is the projection of two closely adjacent principal planes. The entire system is composed of such pairs of planes, the imaginary middle planes of which lie over one another at equal distances.

There are some interesting special cases of this system. If the 12-pointer rings be reduced to simple hexagons,

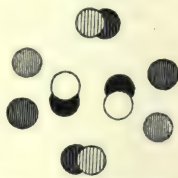


FIG. 517.—Sohncke's Nos. 53, 54, and 55.



**No. 54. The Rhombic Dodecahedral Twelve-pointer System.**—This originates out of the system of the oblong octahedron No. 10. Three such systems—in which the centres of the equifaced tetrahedra now form a centred-cube space-lattice, No. 2 (Fig. 453), instead of the oblong octahedral space-lattice No. 11 (Fig. 466)—are inserted interpenetratingly within one another in three perpendicular directions, so that three equifaced tetrahedra always have the same middle point and therefore form a 12-pointer. The system thus consists of congruent parallel 12-pointers, such as that shown in Fig. 517, the centres of which form a centred-cube space-lattice, No. 2. It may be called rhombic dodecahedral, as the eight cube corners, together with the centres of the six adjacent cubes, form the corners of a rhombic dodecahedron.

**No. 55. The Octahedral Twelve-pointer System.**—This originates out of the rhombic octahedral system No. 8. Three such systems—in which the centres of the equifaced tetrahedra now form a regular octahedral space-lattice, No. 3 (Fig. 454) (that of the centred-face cube), instead of the centred rhombic prism space-lattice No. 9 (Fig. 464)—are inserted interpenetratingly through one another in three perpendicular directions (those of the octahedral axes), so that the three tetrahedra all have the same centre, thus forming the 12-pointer. Hence, the system consists of congruent parallel 12-pointers, such as that represented in Fig. 517, the centres of which form the space-lattice of the face-centred cube.

**Special Cases of the Twelve-pointer Systems 53, 54, and 55.**—The three 12-pointers become the three cubic space-lattices (those of the cube, the centred cube, and the face-centred cube) when they concentrate on and into their centres. As the tetrahedra

can be either right- or left-handed, there are two correspondingly right- and left-handed, enantiomorphous, 12-pointers.

**No. 56. The Regular Compound Two-point Screw System.**

—This is derived from the rhombic counter-screw system No. 11. There are three such systems, the rhombs of which are now

converted into squares with diagonals equal to half the screw-height, inserted through one another in three perpendicular directions, namely, those of the square diagonals and the screw-axis. The axes of three adjacent compound two-point screws run without intersection between one another, situated as if they were the three independent mutually perpendicular edges of a cube. The three part-systems are shown separately in Fig. 518 for the sake of clearness.

**No. 57. The Regular Alternating Two-point Screw System.**—This originates from No. 13, the

alternating rectangular two-point screw system of the second kind. There are three of the No. 13 systems inserted through one another in three perpendicular directions, those of the cube edges, so that the axes of three adjacent two-point screws run between one another without intersection. The rectangles of No. 13 are now squares and the parallelepipedal meshes are cubes; the three axes just referred

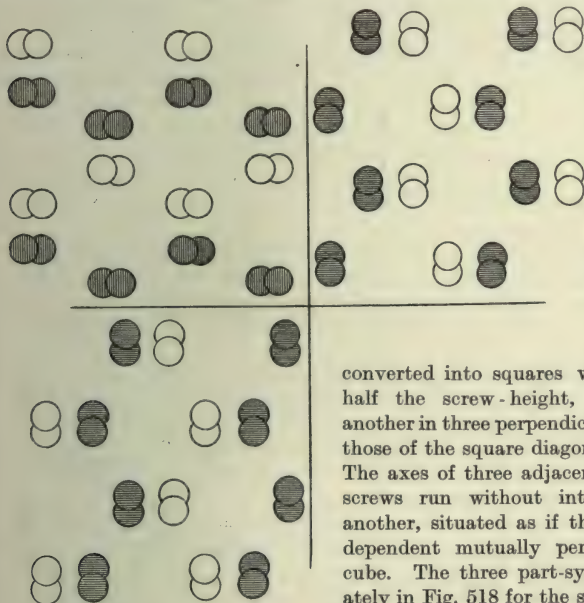


FIG. 518.—Sohncke's No. 56.

to resemble the edges of a cube as regards their situation and mutual relationship. The three part-systems are again drawn separately in Fig. 519.

**No. 58. The Cubic Twenty-four-pointer System.**—This originates out of the compound tetragonal prism system No. 35. There are three such systems—the prism-centres of which form a cubic space-lattice, No. 1 (Fig. 452)—inserted through one another in the three perpendicular directions of the cube edges; so that three prism axes always intersect rectangulary at a common point,

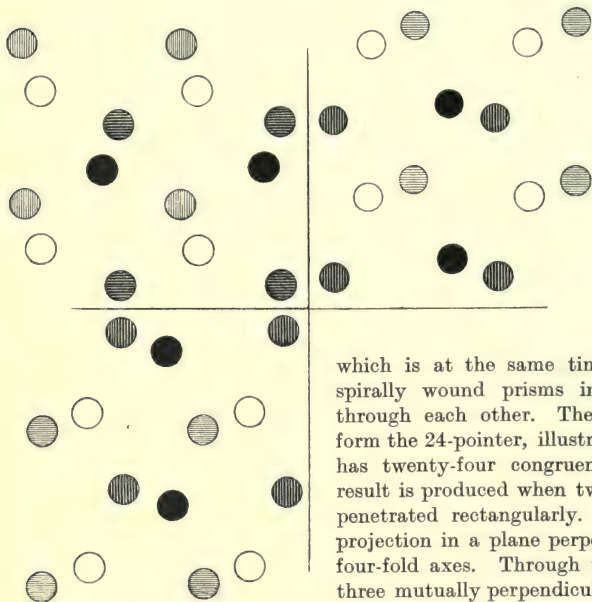


FIG. 519.—Sohncke's No. 57.

which is at the same time the centre of three spirally wound prisms inserted perpendicularly through each other. Their twenty-four corners form the 24-pointer, illustrated in Fig. 520, which has twenty-four congruent corners. The same result is produced when two 12-pointers are interpenetrated rectangulary. The figure shows the projection in a plane perpendicular to one of the four-fold axes. Through the centre, besides the three mutually perpendicular four-fold axes, there also pass four three-fold rotation axes, traversing the middle of the octants. The system thus

consists of congruent parallel 24-pointers, the centres of which form a cubic space-lattice, No. 1 (Fig. 452 on page 583).

**No. 59. The Rhombic Dodecahedral Twenty-four-pointer System.**—This system originates out of system No. 36. Three of No. 36 are inserted through each other along three perpendicular directions, so that three four-fold axes stand always perpendicularly on one another at a common point of intersection, which is then the middle point of a 24-pointer, similar to that shown in Fig. 520. As a 24-pointer originates for every spirally wound column of No. 36, and the tetragonal net becomes cubic in this system, the entire system consists of congruent parallel 24-pointers, the centres of which form a centred-cube space-lattice, No. 2 (Fig. 453 on page 583), that of the rhombic dodecahedron.

**No. 60. The Octahedral Twenty-four-pointer System.**—This also originates out of the compound tetragonal octahedral system No. 36. The centres of all the spirally wound columns form a centred tetragonal column, the height of which is  $\sqrt{2}$  times that of the side of the base, and which is, therefore, a regular octahedral space-lattice, No. 3, six adjacent centres forming the corners of a regular octahedron. Thus three part-systems are inserted through one another in three perpendicular directions, so that three spirally wound columns always have the same centre and form a 24-pointer, as already illustrated in Fig. 520. The entire system consists of congruent parallel 24-pointers, the centres of which form a face-centred cubic space-lattice, No. 3 (Fig. 454 on page 583), which is that of the regular octahedron.

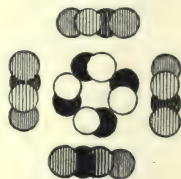


FIG. 520.—Sohncke's Nos. 58, 59, and 60.

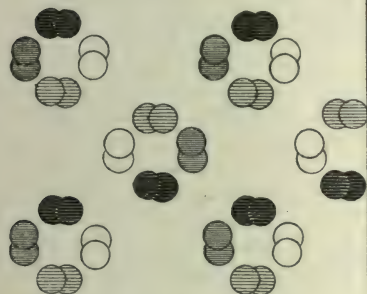
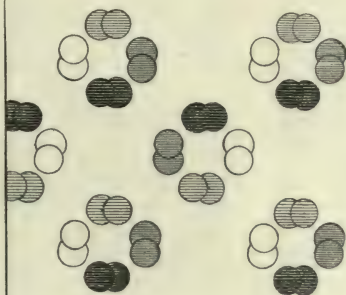
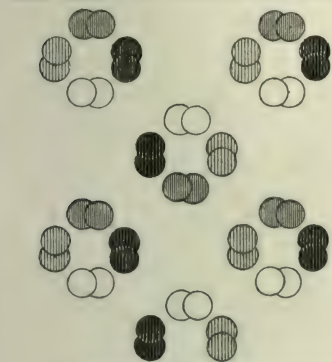


FIG. 521.—Sohnecke's No. 61.

There are three important special cases of the 24-pointers, namely, those formed when they (Nos. 58, 59, and 60 respectively) become reduced to and concentrate on their centres and thereby form the three cubic space-lattices Nos. 1, 2, and 3. The 24-pointers, just like the 12-pointers, may also be of two enantiomorphous types, mirror-images of each other.

**No. 61. The Regular Counter-screw System of the First Kind.**—This system,

represented in Fig. 521, originates out of the four-fold compound counter-screw system No. 33. Three such systems are inserted through one another along three perpendicular directions, so that three adjoining and mutually perpendicular principal axes are arranged like the edges of a cube.



**No. 62. The Regular Counter-screw System of the Second Kind.**—This system,

shown in Fig. 522, likewise originates out of No. 33, three of these being inserted through each other in three perpendicular directions, and also so that three adjacent mutually perpendicular axes lie as if they were cube edges. But the arrangement differs from that of the first kind, No. 61, by the fact that two of the three rectangular directions in question are

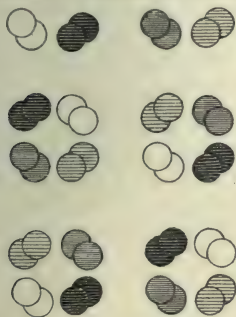


FIG. 522.—Sohnecke's No. 62.



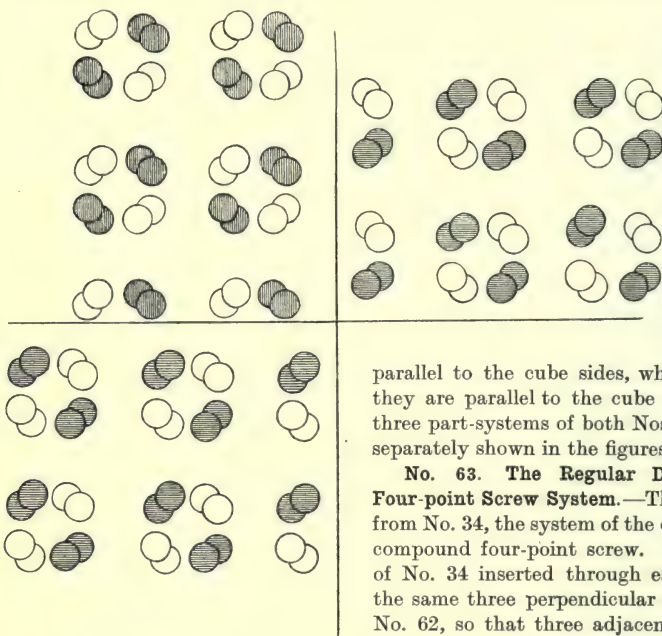


FIG. 523.—Sohncke's No. 63.

parallel to the cube sides, whereas in No. 61 they are parallel to the cube diagonals. The three part-systems of both Nos. 61 and 62 are separately shown in the figures.

**No. 63. The Regular Double-threaded Four-point Screw System.**—This takes its rise from No. 34, the system of the double-threaded compound four-point screw. There are three of No. 34 inserted through each other along the same three perpendicular directions as in No. 62, so that three adjacent and mutually perpendicular screw-axes act as if they were

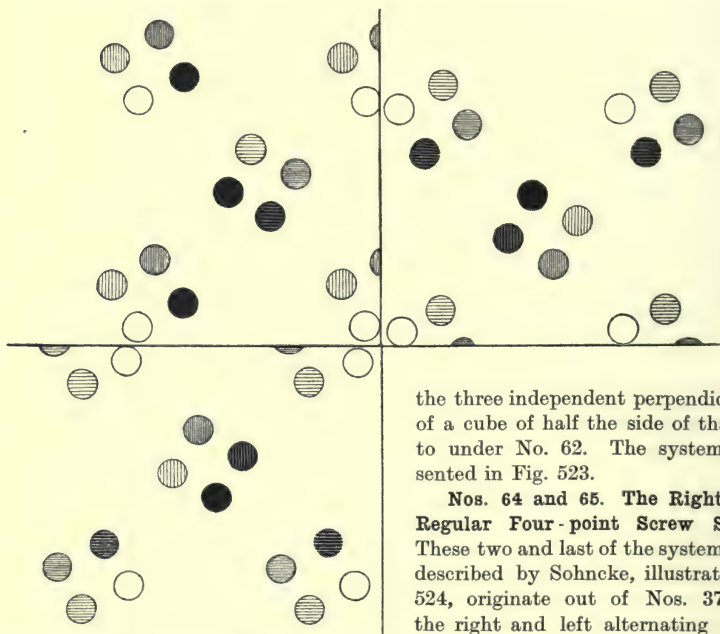


FIG. 524.—Sohncke's Nos. 64 and 65.

the three independent perpendicular edges of a cube of half the side of that referred to under No. 62. The system is represented in Fig. 523.

**Nos. 64 and 65. The Right and Left Regular Four-point Screw Systems.**—These two and last of the systems of points described by Sohncke, illustrated in Fig. 524, originate out of Nos. 37 and 38, the right and left alternating four-point screw systems. They consist of three such

systems, interpenetratingly combined. None of the axes of the three intersect one another, but all are separated by distances equal to a quarter the screw-height. Three principal adjacent axes are always arranged similarly to the three edges of a cube. The position of the principal axes differs according as the system is a right-handed or a left-handed one, their arrangement corresponding to the mode of winding of the screws.

This chapter will now conclude with a table showing the manner in which the 65 Sohncke regular point-systems are distributed among the 32 classes of crystals. The class number is given in the first column, and corresponds exactly to the numbering of the classes on pages 137-39 and in the descriptive Chapters X.-XXII. The last-numbered class in each system is the holohedral class. In the second column is given the symbol, referring to the coincidence-movements which are characteristic, employed by Schönflies to designate and describe the class and its symmetry. The large central column gives the Sohncke regular point-systems, and besides the numbers and names of the actual systems themselves, in their respective classes, an indication is given of the manner in which these point-systems are regarded by Sohncke, when specialised and duplicated or otherwise multiplied, as explaining also the nature of other classes of symmetry than those to which the particular Sohncke systems in their general form directly apply. In the last column is given the distribution among the 32 crystal classes of the whole 230 types of homogeneous structures as conceived by Schönflies, and termed by him "Space-Groups." Schönflies does not number his space-groups consecutively, nor does he give pictures of them.<sup>1</sup> The figures express the total number of the space-groups in each crystal class; but they are subdivided in accordance with the space-lattice which underlies the space-group, in all cases where more than one space-lattice is concerned in the class.

The space-lattice is indicated by the Greek capital letter  $\Gamma$ , to which a characterising suffix is added to indicate the crystal-system; thus  $\Gamma_{tr}$  means triclinic space-lattice,  $\Gamma_m$  monoclinic sp.-l.,  $\Gamma_r$  rhombic sp.-l.,  $\Gamma_t$  tetragonal sp.-l.,  $\Gamma_c$  cubic sp.-l., and as regards the two trigonal and rhombohedral space-lattices Nos. 6 and 7, the former of which is also applicable to the hexagonal system, the Schönflies symbols respectively are  $\Gamma_h$  and  $\Gamma_{rh}$ . As in all but the triclinic and hexagonal systems (and also two classes of the trigonal system) more than one space-lattice corresponds to the crystal-system, the individual space-lattices of the same system after the first are indicated by a dash or dashes affixed above and after the  $\Gamma$ .

Thus not only does the table give the number of space-groups which there are in the crystal class, but it divides them up among the space-lattices which underlie their symmetry. This is also equivalent to classifying them according to their translation groups. The total number of space-groups for the whole crystal-system is also appended on the extreme right of the table, and on adding these together, or all the individual numbers, the total number of space-groups, or types of homogeneous structures applicable to crystals, will be found to be 230.

<sup>1</sup> An account of the 230 types as developed by Schönflies, together with some illuminating drawings, is given by H. Hilton in chapters xviii. to xxiii. of his *Mathematical Crystallography and the Theory of Groups of Movements* (Clarendon Press, Oxford, 1903).

DISTRIBUTION OF THE 65 SOHNCKE REGULAR POINT-SYSTEMS AND OF THE 230  
SCHÖNFLIES SPACE-GROUPS AMONG THE 32 CRYSTAL CLASSES.

Crystal Class.	Schönflies Class-Symbol.	Sohncke System.	Numbers of Schönflies Space-Groups in Classes and Systems.			
		<i>Triclinic System.</i>	$\Gamma_{tr}$ .	Total.		
1	$C_1$	No. 1 multiplied	1	} 2		
2	$S_2$	No. 1, Triclinic space-lattice	1			
		<i>Monoclinic System.</i>	$\Gamma_m, \Gamma_m'$ .			
3	$S$	{ Nos. 2, 3, and 4 multiplied, but with only symmetry plane acting }	2	2	} 13	
4	$C_2$	{ Nos. 2, 3, and 4 multiplied, but with only two-fold axis acting }	2	1		
5	$C_2^h$	{ No. 2, Two-fold prism No. 3, 2-Point screw No. 4, Clinorhombic prism }	4	2		
		<i>Rhombic System.</i>	$\Gamma_r, \Gamma_r', \Gamma_r'', \Gamma_r'''$ .			
6	$V$	{ Nos. 5 to 13, but construction point not in a symmetry plane }	4	2	1	2
7	$C_2^v$	{ Nos. 5 to 13 multiplied and specialised Nos. 2, 3, and 4 multiplied and specialised No. 5, Rectangular prism No. 6, Compound rectangular 2-point screw No. 7, Rhombic prism No. 8, Rhombic octahedron No. 9, Compound rhombic 2-point screw No. 10, Oblong octahedron No. 11, Rhombic counter-screw No. 12, Alternating rectangular 2-point screw of first kind No. 13, Alternating rectangular 2-point screw of second kind }	10	7	2	3
8	$V^h$		16	6	2	4
		<i>Tetragonal System.</i>	$\Gamma_t, \Gamma_t'$ .			
9	$C_4$	{ No. 25, Right 4-point screw No. 26, Left 4-point screw No. 27, Four-fold counter-screw Nos. 28 to 40 multiplied }	4	2	} 68	
10	$S_4$	{ Nos. 2, 3, and 4 tetragonally specialised and multiplied No. 31, Right compound 4-point screw No. 32, Left compound 4-point screw No. 33, Four-fold compound counter-screw No. 37, Right alternating 4-point screw No. 38, Left alternating 4-point screw Also Nos. 34 to 40 multiplied }	1	1		
11	$D_4$	{ No. 28, Double-threaded 4-point screw No. 29, Tetragonal prism No. 30, Tetragonal octahedron Nos. 28 to 30 and 34 to 40 specialised and multiplied }	8	2		
12	$C_4^h$	{ Nos. 5, 7, 8, and 10 specialised No. 34, Double-threaded compound 4-point screw No. 35, Compound tetragonal prism No. 36, Compound tetragonal octahedron No. 39, Alternating double-threaded 4-point screw No. 40, Alternating tetragonal prism }	4	2		
13	$C_4^v$		8	4		
14	$S_4^u$		8	4		
15	$D_4^h$		16	4		
Carry forward						

142



Crystal Class.	Schönflies Class-Symbol.	Sohncke System.	Numbers of Schönflies Space-Groups in Classes and Systems.	
		Brought forward		Total. 142
		<i>Trigonal System.</i>	$\Gamma_{rh}, \Gamma_h.$	
16	$C_3$	{ No. 14, Right 3-point screw No. 15, Left 3-point screw No. 17, Rhombohedron Also Nos. 16, and 18 to 24; specialised }	1 3	30
17	$C_3^i$	{ No. 21 doubled symmetrically No. 18, Right compound 3-point screw No. 19, Left compound 3-point screw No. 20, Compound trigonal prism No. 21, Compound rhombohedron No. 22, Right alternating 3-point screw No. 23, Left alternating 3-point screw No. 24, Alternating trigonal prism }	1 1	
18	$D_3$	{ No. 16, Trigonal prism Nos. 17 and 21 specialised, and latter multiplied No. 21, with construction point in a plane perpendicular to a lateral axis and containing the principal axis Nos. 20 and 24 specialised as regards construction point }	1 6	
19	$C_3^h$		- 1	
20	$C_3^v$		2 4	
21	$D_3^d$		2 4	
22	$D_3^h$		- 4	
		<i>Hexagonal System.</i>	$\Gamma_h.$	
23	$C_6$	{ No. 41, Right 6-point screw No. 42, Left 6-point screw No. 43, Right double-threaded 6-point screw No. 44, Left double-threaded 6-point screw Nos. 45 and 46 multiplied No. 47, Right compound 6-point screw No. 48, Left compound 6-point screw No. 49, Right double-threaded compound 6-point screw No. 50, Left double-threaded compound 6-point screw No. 51, Triple-threaded compound 6-point screw No. 52, Compound hexagonal prism No. 45, Triple-threaded 6-point screw No. 46, Hexagonal prism Nos. 45 and 46 multiplied and specialised Also Nos. 51 and 52 multiplied Nos. 51 and 52 with construction point in a symmetry plane of axial group }	6	22
24	$D_6$		6	
25	$C_6^h$		2	
26	$C_6^v$		4	
27	$D_6^h$		4	
		Carry forward		194

Crystal Class.	Schönflies Class-Symbol.	Sohncke System.	Numbers of Schönflies Space-Groups in Classes and Systems.	
		Brought forward		Total. 194
		<i>Cubic System.</i>	$\Gamma_c, \Gamma_c', \Gamma_c''$ .	
28	T	{ No. 56, Regular compound 2-point screw No. 57, Regular alternating 2-point screw }	2 1 2	36
29	O	{ No. 61, Regular counter-screw of 1st kind No. 62, Regular counter-screw of 2nd kind No. 64, Right regular 4-point screw No. 65, Left regular 4-point screw Also Nos. 58-63, when construction point is not in symmetry plane of axial group }	4 2 2	
30	$T^h$	{ No. 53, Cubic 12-pointer No. 54, Rhombic dodecahedral 12-pointer No. 55, Octahedral 12-pointer (Construction point in all three cases in one of 3 perpendicular symmetry planes of axial group.) }	3 2 2	
31	$T^d$	{ Nos. 53, 54, and 55, with construction point in one of the 6 equal symmetry planes of axial group }	2 2 2	
32	$O^h$	{ No. 58, Cubic 24-pointer No. 59, Rhombic dodecahedral 24-pointer No. 60, Octahedral 24-pointer No. 63, Regular double-threaded 4-point screw (Construction point in all cases in a sym- metry plane of axial group.) }	4 4 2	
Grand total of Schönflies space-groups				230

## CHAPTER XXXII

### THE DETERMINATION OF THE DENSITY OF CRYSTALS AND CALCULATION OF VOLUME CONSTANTS THEREFROM

SPECIFIC gravity determinations require to be much more accurately carried out than has hitherto been the case, in order that the results may be of real value for the purpose of calculating the molecular volume and the molecular distance ratios (topic axial ratios). The crystal material employed, moreover, requires to be of the highest possible degree of purity and homogeneity. The most serious and frequent source of error is due either to the presence of cavities containing mother-liquor within the crystals, when the latter consist of pure chemical substances crystallised from solution, or to the presence of impurities and inclusions of foreign material if the crystals are those of a naturally occurring mineral.

There are only two methods of determining the density of crystals with the requisite degree of accuracy, one being the method of the pyknometer or specific gravity bottle (assuming only the most delicate and accurate form of pyknometer to be employed), within which the powdered crystals are introduced, the bottle being filled up by an inert liquid of known density; the other is the method which we owe to Retgers, of immersion of the crystal, whole and unpowdered, in a liquid of the same density, prepared by diluting a heavy liquid such as methylene iodide to the correct density with a lighter miscible liquid such as benzene.

The latter method is preferable, as the crystal is preserved intact and uninjured, whenever small and perfectly transparent crystals are available the density of which is not superior to that of methylene iodide, 3.33. The heaviest crystal, that is, the one yielding the highest result for the specific gravity, is taken as affording the nearest approach to the truth, its greater density being assumed to be due to its superior freedom from cavities. When the density of the crystal is higher than that of methylene iodide, the pyknometer method is alone available, and the highest result is again taken for a similar reason. When the care and the precautions to be now described are taken, the highest result of the pyknometer method is usually found to agree very closely with the mean result afforded by several determinations with the heaviest crystal by the immersion method, in cases where both methods



are available, several such cases having been very thoroughly tested by the author.

**The Pyknometer Method.**—The form of pyknometer employed and recommended by the author is shown in Fig. 525, which represents the duplicate pair actually used in all the author's investigations. Each is an ordinary specific gravity bottle of 10 c.c. capacity, with an especially accurately ground stopper centrally perforated throughout its vertical length by a capillary bore. A cap has been blown to fit over the stopper, and ground to make excellent contact with the upper conically ground exterior of the neck of the bottle; it is maintained pressed down into position by a spring forming part of a little supporting brass-wire stand, which affords the means of moving the bottle to and from the desiccator and balance without contact with the hand.

Carbon tetrachloride,  $\text{CCl}_4$ , is the liquid employed by the author,



FIG. 525.  
Duplicate Pyknometers with  
Caps.



FIG. 526.  
Vacuum-receiver for Exhaustion  
of Pyknometers.

the chief advantages which it possesses being freedom from action on all the crystalline salts hitherto dealt with, combined with great permanence in a state of purity. The use of the cap is to prevent evaporation of the carbon tetrachloride from either the neck or the capillary, both of which are enclosed within the cap. Many forms of pyknometer, and many variations of the pyknometer method, have been tried by the author, but the method of the capped pyknometer is infinitely superior to any other. It is an advantage to employ a pair of these capped pyknometers simultaneously, affording two distinct determinations, carried out under identical conditions. Such a pair are shown in Fig. 525, standing on a glass plate which forms the base of a glass protecting cover, the whole acting as a desiccator, a dish of vitriol being included to maintain a dry atmosphere. When it is intended to use the pyknometers, they should be thoroughly cleaned if not already so (this should obviously be done immediately after every determination, leaving them clean for the next), and allowed to stand in their wire supports under the glass cover-vase for a sufficient length of time (a quarter of an hour is a good time) to recover surface

equilibrium; they may then be weighed on the most accurate balance available, such as the most delicate Sartorius short beam balance. The weights should have been standardised, and be preferably platinised, or of platinum throughout, not merely those below one gramme which are always made of platinum.

Such a quantity of the powdered crystals should be employed as occupies about one-third or at most not more than one-half of the capacity of the bottle in each case, in order to obtain the best results, the rest of the space being filled up with carbon tetrachloride. The pulverisation of the crystals, and the filling of the bottle with the powder and carbon tetrachloride, are very important operations, the accuracy of the determinations depending largely on the care taken with them. A perfectly clean agate mortar should be employed, and the powder sifted through the very finest platinum gauze before it is accepted as adequately pulverised. Moreover, as the powdering frees the mother-liquor from such cavities as are broken into, the powder invariably requires careful drying before transference to the bottles. The temperature at which the drying can occur with safety depends, of course, on the nature of the crystalline substance. In the case of the anhydrous sulphates of the alkalis, potassium sulphate for instance, it may be well over  $100^{\circ}$  C., and as high as  $150^{\circ}$ , a copper air-bath being employed. In the case of salts containing water of crystallisation, such as ammonium magnesium sulphate with  $6\text{H}_2\text{O}$ , a temperature only very slightly superior to the ordinary atmospheric can with safety be employed. After drying, it is advisable to powder the material again in the mortar and to resift through the platinum gauze.

After transferring the proper amount of the powdered crystalline substance to the two pycnometers, the interior of the necks must be well cleared of powder with a little silk cloth, the stoppers inserted, the caps adjusted, and the whole placed in the wire stand in each case. The two stands with their bottles are then allowed to rest in the desiccator for the usual interval. They are then to be each separately weighed, just as they are, stand included. The weight of the bottles in their stands when empty being known, from previous weighings (confirmed before each determination), the additional weight in each case is that of the salt introduced. The bottles are then opened again, and sufficient carbon tetrachloride is poured in to cover well the powder and about two-thirds fill the bottle in each case, not more, or some may be forced out by bubbles during evacuation. The bottles themselves, without stoppers, caps or stands, then require to be placed in a Sprengel vacuum, in order to extract the air imprisoned between the grains of the powder, which would otherwise cause a grave error. A receiver of the minimum size necessary to take the two bottles simultaneously is conveniently employed; the one used by the author is further reduced in capacity by a solid wooden stand for the two bottles, which just fits inside it, occupying nearly one-third of its volume. It is shown in Fig. 526. As the pump is worked, and the air rises in bubbles and is rapidly removed by the pump, the exterior of the receiver requires to be gently

tapped to assist in releasing the bubbles as soon as possible after they make their appearance in the carbon tetrachloride; for otherwise they might accumulate and force the liquid into the neck or even out of the bottle. Eventually, when the vacuum gets adequately high and the

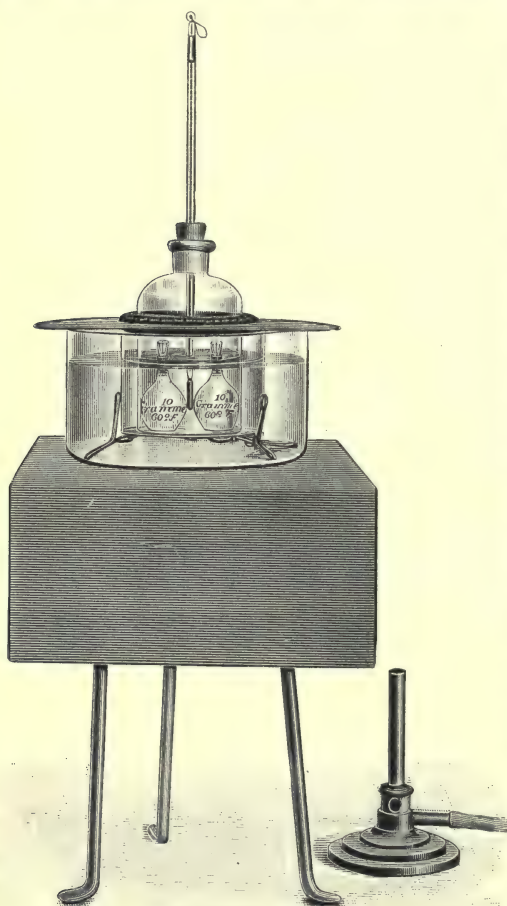


FIG. 527.—Double Water-bath in which Pyknometers are warmed to 20°.

It is convenient to determine the specific gravity at the uniform temperature of 20° C., and all the author's published density determinations have referred to this temperature. The water-bath with the pyknometers immersed in it is shown in Fig. 527. It consists of three glass vessels one inside another, an outer dish containing water, an inner one resting on a wire stand to keep it from touching the outer dish, and also containing water to the height which will enable the full bottles to rest in it with the upper part of their necks just emerging,

drops of mercury falling down the long tube of the pump begin to click, the carbon tetrachloride commences to boil, and its vapour effectually expels the last traces of air. When the boiling has proceeded for a few minutes, with frequent tappings of the receiver, it will usually be the case that all air is finally got rid of from below the surface of the liquid. The outside air may then be readmitted into the receiver and the bottles removed. They are then to be filled up with carbon tetrachloride, the stoppers inserted but without caps, taking great care to avoid enclosing any bubbles of air, and immersed in a water-bath up to near the tops of their necks, in order that the bottles may be raised to the temperature at which the content of each bottle is to be determined, and for which the density of the salt is to be ascertained.



and an innermost small bell-jar, through a niched caoutchouc stopper in the tubular neck of which the thermometer is inserted, with the centre of its bulb at the height of the widest part of the bottles and between the two latter, the diameter of the bell-jar being ample to admit both bottles within it. The outer bath rests on a metal plate, turned down at the edges and supported on a tripod stand. By placing a very small Bunsen flame underneath the metal plate for short periods at a time the temperature of the baths may be brought very slowly up to  $20^{\circ}$ , so slowly that there is full certainty of the pyknometers taking the temperature of the inner bath as indicated by the thermometer. The latter should read directly to  $0.1^{\circ}$  C., and must be one the readings of which for  $0^{\circ}$  and  $100^{\circ}$  have been recently verified, by the usual method of immersion in ice and steam, and any necessary corrections to which have been accurately determined. Its indications are read by means of a telescope arranged horizontally a yard or more away at the same level, in order that no error of parallax may be incurred, due to eye-reading at close quarters.

As the temperature rises the carbon tetrachloride continues to ooze out of the capillary bore of the stopper of each pyknometer. When  $20^{\circ}$  is reached, the last half-degree of rise having occupied ten minutes or so, the drops of carbon tetrachloride standing over the capillaries are brushed off, and the bottles are simultaneously removed from the bath, and carefully wiped with a clean handkerchief without touching them with the fingers, the liquid having already receded down the capillary owing to contraction in the colder air. The caps are then put on, the pyknometers fitted into their wire stands, and the pair placed in the desiccator and allowed to rest for the usual few minutes to take up equilibrium of surface conditions. They are then weighed in their stands, at the ordinary temperature of the room.

The wiping off of the drop of carbon tetrachloride from the top of each stopper must be done with precision and nicety, immediately before, and indeed as nearly as possible at the instant of, removal of the bottle from the bath; for otherwise, as the cooling down to the temperature of the outside air causes the liquid within the bottles to contract and recede down the capillary, some of that contained in the drop will re-enter the pyknometer. The best plan is to sweep off the drop with a finger of one hand at the instant the pyknometer is removed with the other hand, and to complete the wiping after the second pyknometer has been similarly treated, and the liquid in the capillary has receded a little way down the bore, away from any slight trace remaining on the stopper end; for by this course the object is accomplished without any risk of expansion, due to the proximity of the warm hand, causing any carbon tetrachloride to exude, any such slight expansion being then inadequate to bring the liquid again to the top of the capillary bore.

After the weighing they may be again filled up with carbon tetrachloride, and the process of warming to  $20^{\circ}$  again gone through; the water-bath will have cooled down adequately in all probability during the weighing, or if not a little cold water can be added to it to bring it

down to a good starting temperature two or three degrees below  $20^{\circ}$ . After removal of the bottles at exactly  $20^{\circ}$  as before, cleansing, capping, and fitting in their stands, they are to be allowed to stand again for the usual short interval and then once more weighed. The taking of two sets of weighings thus minimises any error due to the correct attainment of  $20^{\circ}$  or to the circumstances of the wiping of the drop, while the employment of a pair of pyknometers minimises other errors such as those due to any residual air inclusion.

Many crystalline salts are more or less deliquescent, and the property is particularly emphasised when the crystals are powdered, owing to the immense surface then presented to the moisture of the air. In order to prevent error from this cause, and to render the accuracy of the determinations in such cases as perfect as for crystals with no tendency to absorb moisture,

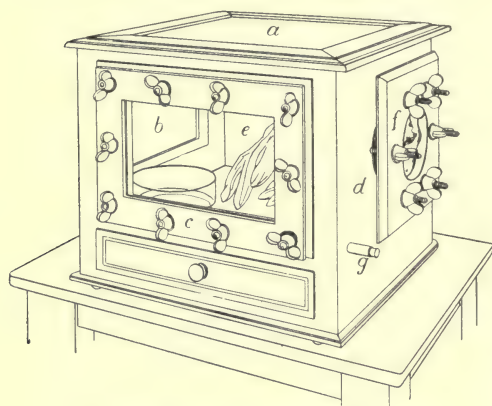


FIG. 528.—Desiccating Chamber for use with Deliquescent Crystals.

the author performs the filling of the bottles with the powder, after it has been dried at a suitable temperature in an air-bath, in the interior of a closed air-tight chamber, a large desiccator in fact of special construction. It is shown in Fig. 528. The manipulation is carried out with the hands placed in a pair of caoutchouc gloves inserted in an air-tight manner through two adjacent sides *d* and *e* of the rectangular mahogany box which constitutes the chamber.

The two other sides *b* and *c* and the top *a* are glazed, so that the manipulator can see what he is doing within. The pyknometers, agate mortar, desiccating dish of oil of vitriol or phosphoric anhydride, the substance powder, and any other required articles, are placed within the box overnight, through one of the sides *c*, generally arranged in front, the large plate-glass window of which is detachable and capable of air-tight fixation again afterwards by a series of bolts with winged nuts, the contact being made absolute between the window frame and the box side by indiarubber facings on both. The gloves are similarly clamped against the two other box sides by means of bolted frames, each having a circular aperture large enough to enable the hand to pass through, and each of which presses a wooden curtain-pole ring on which the glove wrist is stretched and which also is large enough to admit the hand, against an indiarubber pad on the box side, in which latter a corresponding circular aperture has also been cut. The whole box is rendered as air-tight as possible by several coats of varnish, inside and out. Having placed everything necessary in the



box overnight, and hermetically closed the window again, the air within the chamber next morning is found to be adequately dry for the operation of filling the bottles with the powdered salt to be undertaken with safety. The author found the apparatus of great value in the determination of the densities of the very deliquescent selenates of the alkalis. If in any other case it should be desirable to work in an atmosphere of inactive gas such as carbon dioxide or nitrogen, provision is made for filling the chamber with it by the addition of a couple of short brass tubes, on opposite sides (diagonally) of the chamber, one of them being shown at *g*. Under ordinary circumstances these tubes are stoppered and sealed up.

Before commencing a series of density determinations the specific gravity of the liquid, carbon tetrachloride, requires to be most accurately ascertained, for the value of this constant will influence all the determinations of the crystal densities. In order to arrive at this important constant we have first to determine (*a*) how much water (by weight) the pycnometer contains at  $20^{\circ}$ , and then (*b*) to ascertain how much carbon tetrachloride is contained under the same conditions and at the same temperature of  $20^{\circ}$ . The relative density of carbon tetrachloride at  $20^{\circ}$  compared with that of water at  $20^{\circ}$ , afforded by the quotient of the two weights,  $b/a$ , has then to be corrected so as to compare with water at  $4^{\circ}$ , by multiplying by 0.99825, the density of water at  $20^{\circ}$  compared with water at  $4^{\circ}$  taken as unity. The water employed for (*a*) must be pure distilled water which has just previously been freed from air by boiling, and subsequently cooled in a stoppered flask which it fills, in order to minimise any further solution of air. In all the weighings during these operations (*a*) and (*b*), as well as in the subsequent determination (*c*) of the density of the crystalline substance, correction must be made for the air displaced both by the contents of the pycnometer placed on the one pan of the balance, and by the brass weights employed to counterpoise it on the other pan; for the difference of the two displacements is often considerable enough just to affect the third place of decimals, and at any rate to affect considerably the fourth place in the value for the density. It is adequate to take the weight of one cubic centimetre of dry air as 0.0012 gramme, for the usual atmospheric conditions of temperature and pressure. The specific gravity of the brass weights is taken as 8.4, the exterior platinisation not affecting the question, and the volume of the platinum weights used for the decimal places is so inconsiderable that the whole weight on the pan can be taken as of specific gravity 8.4, an approximation which is fully near enough for the purpose, any further refinement not affecting the fourth decimal place of the density value. The density of the carbon tetrachloride and of the crystal powder, for use in calculating the correction in the first determination, before the exact corrected value has been arrived at, may be the uncorrected value in each case; it is safest to consider this as provisional, the correction being subsequently verified (or altered if it should affect the last unit in the fourth place of decimals) when the true value has been determined. For the



second and all subsequent determinations the true specific gravity as afforded by the corrected result of the first determination should, of course, be used.

It has been the author's practice to redetermine the density of the stock of pure carbon tetrachloride, after redistillation (the boiling point at 760 mm. pressure being  $76\cdot7^{\circ}$  C.), before commencing each series of crystal density determinations, that is, before the operations on each group of salts, the determinations for which are to be carried out on successive days during the course of a week or two.

We may now proceed to illustrate the method by an actual example, and cannot do better than take the case of the typical crystalline substance the goniometry of which was worked through in Chapters IV. and VIII., namely, potassium sulphate,  $K_2SO_4$ . Operations (a) and (b), which are the same whatever the substance or substances to be investigated, and (c), which is similar for all substances but not identical, will each be worked through in duplicate, that is, for the two pycnometers, which we may label Nos. 1 and 2 respectively. The weights (in grammes) will be set out in the order in which the weighings were made. By weight of pycnometer is to be understood in all cases that of the capped bottle in its wire stand.

(a) DETERMINATION OF WATER CONTENT.

*Experimental Data.*

	Pyk. No. 1.	Pyk. No. 2.
Weight of pycnometer . . . . .	16·4539	18·6834
Do. and water (as filled at $20^{\circ}$ ) . . . . .	26·4262	28·6636
Apparent weight of water content for $20^{\circ}$ . . . . .	9·9723	9·9802

*Calculations.*

True weight of water content of No. 1 for $20^{\circ} = 9\cdot9723 + [0\cdot0012 \times (10\cdot0 - 1\cdot2)]$		
		8·8
	$= 9\cdot9723 + 0\cdot0106$	
	$= 9\cdot9829$	
Do. do. No. 2 do.	$= 9\cdot9802 + 0\cdot0106$	
	$= 9\cdot9908$	

The correction for air displaced, the expression in square brackets, is the same for both determinations, the pycnometers each holding 10·0 c.c., when the volume is expressed to one place of decimals, which is enough for the purposes of the calculation of this correction. The 10 c.c., however, have to be diminished by the volume of the weights on the other pan, which is got by dividing 9·9723 and 9·9802 respectively by the specific gravity 8·4 of the weights, and which works out to 1·2 in each case. Hence 8·8, the difference of 10 c.c. and 1·2 c.c., multiplied into the weight of 1 c.c. of air, 0·0012 gramme, gives 0·0106 gramme for the weight to be added to the apparent weight in order to arrive at the true weight of the water content.

(b) DETERMINATION OF DENSITY OF CARBON TETRACHLORIDE.

*Experimental Data.*

	Pyk. No. 1.	Pyk. No. 2.
Weight of pycnometer . . . . .	16·4539	18·6834
Do. and $CCl_4$ (as filled at $20^{\circ}$ ) . . . . .	32·3120	34·5515
Apparent weight of $CCl_4$ content for $20^{\circ}$ . . . . .	15·8581	15·8681

*Calculations.*

$$\begin{aligned}
 \text{True weight of CCl}_4 \text{ content of No. 1 for } 20^\circ &= 15.8581 + [0.0012 \times (10.0 - 1.9)] \\
 &8.1 \\
 &= 15.8581 + 0.0097 \\
 &= 15.8678. \\
 \text{Do.} \quad \text{do.} \quad \text{No. 2 do.} &= 15.8681 + 0.0097 \\
 &= 15.8778
 \end{aligned}$$

The correction for air displaced is again the same for both determinations, the volume of air displaced by the  $\text{CCl}_4$  being 10.0 c.c. and that by the weights 1.9 c.c. (15.86 divided by their sp. gr. 8.4), the difference which has to be taken into consideration being 8.1 c.c.

We now know the content of both pure water and carbon tetrachloride at  $20^\circ$  for each pyknometer, and the quotient of the latter by the former is the specific gravity of carbon tetrachloride at  $20^\circ$  compared with water at  $20^\circ$ . We have now to convert it, however, to the denser standard of water at  $4^\circ$  by multiplying by the density of water at  $20^\circ$  compared with its maximum density at  $4^\circ = 1$ , namely, by 0.99825.

$$\begin{aligned}
 \text{Sp. gr. of CCl}_4 \text{ at } 20^\circ/4^\circ &= \frac{15.8678}{9.9829} \times 0.99825 = 1.5867 \text{ by pyknometer No. 1,} \\
 \text{and} &= \frac{15.8778}{9.9908} \times 0.99825 = 1.5865 \text{ by pyknometer No. 2.}
 \end{aligned}$$

A third determination of the density of carbon tetrachloride was also made with a larger pyknometer of 30 c.c. capacity, and the value 1.5867 was obtained, identical with the value from No. 1. Any slight error in any of these determinations being in all probability on the side of lowness, owing to the much greater volatility of carbon tetrachloride than water, the higher value is probably nearer the truth than the lower. Hence, as we have the confirmation by the third determination, the higher value 1.5867 is accepted as the density of carbon tetrachloride for  $20^\circ/4^\circ$ .

## (c) DETERMINATION OF DENSITY OF POTASSIUM SULPHATE.

*Experimental Data.*

		Pyk. No. 1.	Pyk. No. 2.
Weight of pyknometer		16.4537	18.6834
Do.	and $\text{K}_2\text{SO}_4$	21.7144	23.1336
Do.	do. and $\text{CCl}_4$ (as filled at $20^\circ$ )	34.4364	36.3538
Apparent weight of $\text{K}_2\text{SO}_4$ in bottle		5.2607	4.4502
Do.	$\text{CCl}_4$ do. (when full at $20^\circ$ )	12.7220	13.2202

*Calculations.*

$$\begin{aligned}
 \text{True weight of K}_2\text{SO}_4 \text{ in pyk. No. 1} &= 5.2607 + [0.0012 \times (2.0 - 0.6)] \\
 &1.4 \\
 &= 5.2607 + 0.0017 = 5.2624. \\
 \text{Do.} \quad \text{No. 2} &= 4.4502 + [0.0012 \times (1.7 - 0.5)] \\
 &1.2 \\
 &= 4.4502 + 0.0014 = 4.4516. \\
 \text{True weight of CCl}_4 \text{ in pyk. No. 1} &= 12.7220 + [0.0012 \times (8.0 - 1.5)] \\
 &6.5 \\
 &= 12.7220 + 0.0078 = 12.7298. \\
 \text{Do.} \quad \text{No. 2} &= 13.2202 + [0.0012 \times (8.3 - 1.6)] \\
 &6.7 \\
 &= 13.2202 + 0.0080 = 13.2282.
 \end{aligned}$$

	Pyk. No. 1.	Pyk. No. 2.
Weight of full $\text{CCl}_4$ content for $20^\circ$ from (b) . . . . .	15.8678	15.8778
Weight of $\text{CCl}_4$ displaced by $\text{K}_2\text{SO}_4$ at $20^\circ$ . . . . .	3.1380	2.6496

This last is the difference between the weight of the content of the bottle when full of  $\text{CCl}_4$  alone and of the  $\text{CCl}_4$  in the pyknometer along with  $\text{K}_2\text{SO}_4$  when full, that is, the difference between the two previous items.

Hence, at  $20^\circ$ , 5.2624 grammes and 4.4516 grammes of potassium sulphate occupy respectively the same bulk as 3.1380 and 2.6496 grammes of carbon tetrachloride. The quotients of the former two numbers respectively by the latter two will afford the relative density of potassium sulphate compared with that of carbon tetrachloride, both at  $20^\circ$ , for the two respective experiments, and as we have found that the density of carbon tetrachloride compared with the standard of water at  $4^\circ$  is 1.5867, the density of potassium sulphate at  $20^\circ$  compared with water at  $4^\circ$  will be as under :

$$\text{Sp. gr. of } \text{K}_2\text{SO}_4 \text{ at } 20^\circ/4^\circ = \frac{5.2624}{3.1380} \times 1.5867 = 2.6609, \text{ by pyknometer No. 1,}$$

$$\text{and } \frac{4.4516}{2.6496} \times 1.5867 = 2.6659, \text{ by pyknometer No. 2.}$$

The corrections for air displaced (again in square brackets) are quite different for the two pyknometers, owing to the amount of salt taken in the two experiments being different; consequently, the amounts of carbon tetrachloride required to fill up the pyknometers are also different, and their corrections different. But the sum of the volumes of the salt and liquid is of course the same in both experiments, namely, the capacity of the pyknometers 10.0 c.c. (2.0 and 8.0 in the case of No. 1, and 1.7 and 8.3 in the case of No. 2); in each case the volume of the salt or liquid has to be diminished by that of the weights on the other pan, obtained by dividing them by their specific gravity 8.4, in order to arrive at the displacement of air which affects the result and which, therefore, requires to be taken into account.

As regards any difference of volume between the pyknometer itself and the weights which counterpoise it, the use of brass for the stand reduces such difference to that merely between the glass bottle, which is very light and thin, and its equivalent weight in brass weights, and this is so relatively small that it is not found to affect the fourth place of decimals, and so it can be neglected. It may be tested by actually using a duplicate bottle as a tare instead of weights corresponding to the weight of the bottle, and thus getting rid altogether of any difference of volume. But the author has not found it necessary to use this method of a tare on other than a few test occasions, as the correction for lack of it has proved to be negligible in the case of results expressed to four places of decimals.

It is absolutely useless to calculate results to more than four places of decimals, as different crops of crystals of the same pure salt often show differences of specific gravity in the third place. Indeed, the only use of the fourth place is to ensure accuracy in the third place of decimals. The actual pair of results just worked out show a difference of five units in the third place. This, however, is about the extreme difference which is ever found with good crystals, and the examples have been chosen to illustrate this fact. Four other determinations which the author carried out with different crops of potassium sulphate crystals yielded results of intermediate value between 2.661 and 2.666. A seventh determination again yielded the highest figure 2.6660.

For the reason already fully specified, that the highest value



obtained represents in all probability the density of the specimen most free from cavity-inclusions of mother-liquor, the value 2.666 has been accepted by the author as the true specific gravity of potassium sulphate at 20°, compared with water at 4°.

**The Retgers Suspension Method.**—The first operation in connection with this method consists in producing such a mixture of pure methylene iodide or other heavy liquid and benzene or other suitable and miscible light liquid, as is of exactly the same density as the heaviest of the small crystals employed, which should be chosen from the best crops on account of their perfect transparency and, therefore, of freedom from visible cavities or inclusions. The author prefers methylene iodide,  $\text{CH}_2\text{I}_2$ , to all other heavy liquids, and benzene to all light ones, and uses the mixture of the two in all cases where neither liquid reacts chemically or as a solvent upon the crystalline substance under investigation. Methylene iodide is almost colourless, only faintly yellow, when first prepared, and is so supplied by any of the first-class manufacturers. It is issued in dark brownish-yellow bottles, and the bottle is best kept in a tin-plate case in the dark, as the liquid becomes orange-coloured after exposure to daylight. Its specific gravity when pure is 3.342 just above its melting point, 5° C., and about 3.33 at the usual temperatures of the air during the experiments. The specific gravity of benzene at 15° is 0.884, so that the mixture of the two liquids in regularly varying relative quantities affords a very wide range of density.

For crystalline salts of higher specific gravity than 3.33, such as the sulphates and selenates of rubidium, caesium, and thallium, there is unfortunately at present no liquid known which is at the same time of adequately high density and without solvent or chemical action on the salts, and recourse is of necessity had to the pycnometer method. Rohrbach's solution, for instance, of specific gravity 3.588, consists of an aqueous solution of 100 parts barium iodide and 130 parts mercury iodide, and of course the water of an aqueous solution dissolves the crystals of the salts of the alkali sulphate and selenate series.

An alternative liquid to methylene iodide which is somewhat more stable is acetylene tetrabromide,  $\begin{array}{c} \text{CHBr}_2 \\ | \\ \text{CHBr}_2 \end{array}$ , the specific gravity of which is 3.001 at 6°. It is prepared by leading acetylene gas into cooled bromine. The author on the whole prefers methylene iodide, as it is much pleasanter to work with, the vapour of acetylene tetrabromide being somewhat irritating. Toluene may be used instead of benzene as the lighter liquid, and in the case of Rohrbach's solution, water is, of course, used as the lighter diluting liquid. This latter solution is to be employed when water is without solvent action while the organic liquids attack or dissolve the crystals under investigation, such as those of related organic compounds, which are often soluble in organic liquids but not in water. Rohrbach's solution may also be used for many minerals, and enables those of densities a little higher than that of methylene iodide to be dealt with.

The author's method of conducting the operations will be elucidated by Fig. 529, which shows the simple apparatus employed.

About 8 c.c. of methylene iodide, supposing this to be the heavy liquid decided on, are transferred to a miniature dropping funnel with cylindrical bulb of about 20 c.c. capacity. The ten or more perfect small crystals which have already been used for the goniometrical work

and have been thereby proved to be of perfect character, and from their careful selection on account of transparency (or other perfections if the substance be opaque) will be particularly suitable for our purpose, being least likely to contain cavities, are introduced and swim on the surface, assuming them to be lighter than methylene iodide. Benzene (or toluene) is then gradually introduced from a still smaller dropping funnel supported above the larger one, until the crystals begin to regain the surface only slowly after agitation of the liquid, when all further additions of benzene are to be made only one drop at a time, followed by vigorous shaking, with the stopper in position. The agitation of the contents of the stoppered vessel can only be efficiently achieved by holding the latter freely in the hand, the neck being the best place to grip it by, between the second finger and thumb, so as to

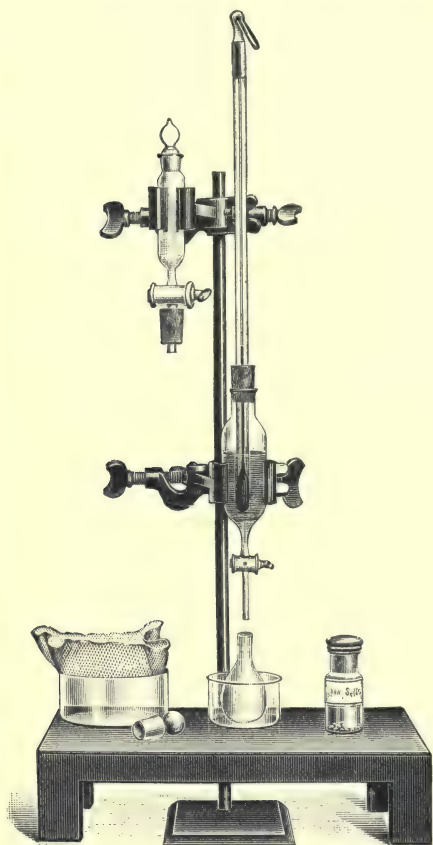


FIG. 529.—Apparatus for Retgers Suspension Method of Density Determination.

avoid warming the liquid, which is prevented from reaching the neck (except as a thin film) by the stopper, the latter being held firmly in position by the first finger. As soon as the desired equilibrium of density is attained, the stopper is replaced by a centrally bored cork carrying a standardised thermometer reading to  $0.1^{\circ}$ , which should be so arranged that its bulb lies altogether immersed in the liquid. When equilibrium of temperature is also attained, the heaviest crystal should float anywhere in the liquid without rising or falling. It need scarcely be

said that before using the crystals for density determinations they should be cleansed from any adhering goniometer wax, which can be readily done with the benzene.

The second operation consists in determining the density of the liquid mixture by weighing a pyknometer filled with it. By working with a pair of pyknometers, the same as have been described in the previous section of this chapter, it can be so arranged that if in the first determination the tendency of the heaviest crystal should be, if anything, to rise, then in the second determination with the other pyknometer (the filling of each pyknometer corresponding to a separate determination) the tendency shall be for the crystal to sink, when it moves at all. Immediately the temperature of the liquid has been read, the latter is run off into one of the pyknometers as quickly as the stopcock allows. It is an advantage to have a small grating of platinum gauze, just smaller than the neck, lying loosely at the bottom of the cylindrical bulb of the funnel; the crystals are then retained above it during the process of running off the liquid into the pyknometer. Otherwise very small crystals may get down into the tap capillary. The perforated stopper of the pyknometer is replaced the moment the latter is full, and the drop on the top swept off; the neck is wiped dry without contact with the warm fingers, the cap fitted on, and the pyknometer inserted in its spring stand, which presses the cap tightly down on the neck. Rapidity is the essence of the process, and the pyknometer is at once weighed, before there is time for the least trace of the very volatile benzene to escape through the cap. All weighings must be corrected for air displaced, precisely as in the pyknometer determinations already described. As the usual time is not allowed for equilibrium of exterior surface condition of the pyknometer, the weight of the empty pyknometer should of course be taken under similar conditions.

It is best to work in a room the temperature of which is as near as possible to  $20^{\circ}$ , the temperature to which all the author's density results are referred. When it differs, it had better be lower than higher, to minimise loss of benzene, but preferably not lower than  $15^{\circ}$ , for all the reductions to the standard of  $20^{\circ}$  have to be made with the aid of the knowledge of the coefficient of expansion of the crystals. Retgers takes this latter to be 0.0001 for salts generally. Fortunately the author has carried out a complete series of determinations of the thermal expansions of the sulphates of the alkalies,<sup>1</sup> the method of which will be described in Chapter LVII., and the results fully agree with Retgers' supposition. The actual coefficients of cubical expansion at any temperature  $t$  were found to be :

For potassium sulphate,  $0.00010475 + 0.0000001396 t$ .

For rubidium sulphate,  $0.00010314 + 0.0000001534 t$ .

For cæsium sulphate,  $0.00010170 + 0.0000001620 t$ .

The correction per degree is, therefore, 0.0001 multiplied by the specific gravity of the salt.

<sup>1</sup> *Phil. Trans.*, 1899, A, 192, 455.



An example will now be given, in conclusion, of a pair of determinations of the density of potassium sulphate by the suspension method. The experiments were carried out in the year 1905; the previous set by the pycnometer method, of which a pair of examples are given earlier in this chapter, were made in 1893. In the meantime the weights of the pycnometers had naturally become reduced somewhat by wear, and No. 2 had lost more owing to the stopper having been ground a little shorter to be the more certain of quite clearing the cap.

The water content had also been redetermined several times, and the latest previous value is now given instead of the older 1893 value.

#### DENSITY OF POTASSIUM SULPHATE BY SUSPENSION METHOD.

##### *Experimental Data.*

	No. 1.	No. 2.
Weight of pycnometer . . . .	16.4522	18.6462
Do. and liquid . . . .	43.0972 at 18.4°	45.3188 at 18.1°
Apparent weight of liquid . . . .	26.6450 „	26.6726 „

##### *Calculations.*

Correcting first the apparent weight of the liquid for the air displaced both by it and by the weights, 10 c.c. being the volume of the liquid and  $26.6/8.4 = 3.2$  being the volume of the weights, we have :

$$\begin{aligned} \text{True weight of liquid in No. 1} &= 26.6450 + [0.0012 \times (10.0 - 3.2)] \\ &\quad \quad \quad 6.8 \\ &= 26.6450 + 0.0082 = 26.6532. \\ \text{Do. do. No. 2} &= 26.6726 + 0.0082 = 26.6808. \end{aligned}$$

If  $t$  be the temperature of the liquid at the moment of transference to the pycnometer, in the above cases 18.4° and 18.1° respectively, then the

$$\text{Specific gravity of liquid at } t^\circ/4^\circ = \frac{\text{Weight of liquid content at } t^\circ}{\text{Weight of water content at } 4^\circ}.$$

Now the

$$\text{Weight of water content at } 4^\circ = \frac{\text{Weight of water content at } 20^\circ \text{ as directly determined}}{\text{Spec. grav. of water at } 20^\circ/4^\circ = 0.99825}.$$

Hence :

$$\text{Spec. grav. of liquid and crystal at } t^\circ/4^\circ = \frac{\text{Wt. of liquid content at } t^\circ \times 0.99825}{\text{Wt. of water content at } 20^\circ}.$$

For the two different experiments this works out as under :

$$\text{For No. 1, Spec. grav. of liquid at } 18.4^\circ = \frac{26.6532 \times 0.99825}{9.9839} = 2.6650;$$

$$\text{For No. 2 do. do. at } 18.1^\circ = \frac{26.6808 \times 0.99825}{9.9917} = 2.6657.$$

These results for the two temperatures of 18.4° and 18.1° have now to be corrected to 20°, the correction being found by multiplying 0.0001 the coefficient of cubical expansion of the crystals by the specific gravity now found, 2.66, and also by the difference of the two respective temperatures from 20°. The values of the two corrections are :

$$\text{For No. 1, } 0.0001 \times 2.66 \times (20 - 18.4) = 0.0004;$$

$$\text{For No. 2, } 0.0001 \times 2.66 \times (20 - 18.1) = 0.0005.$$

Reducing then the specific gravities for  $18.4^{\circ}$  and  $18.1^{\circ}$  respectively by 0.0004 and 0.0005, we obtain for the specific gravity of the liquid, and therefore of the heaviest of the crystals, for  $20^{\circ}/4^{\circ}$ , the following numbers :

From No. 1, 2.6646,

From No. 2, 2.6652.

A further pair of similar determinations with fresh crystals of potassium sulphate yielded for the heaviest individual the values 2.6640 and 2.6652 for  $20^{\circ}/4^{\circ}$ . The mean of the two determinations for the heaviest crystal of the first batch is 2.6649, and that of the pair of estimations with the heaviest crystal of the second batch is 2.6646. Hence, accepting the former pair as having been conducted with the crystal of maximum heaviness, the final result of the determination of the specific gravity of potassium sulphate crystals by the suspension method may be taken as 2.665. Indeed, both pairs of determinations afford this same value when expressed to three places of decimals.

The highest result of the determinations by the pycnometer method has been shown to be 2.666, and as the higher figure is more likely to be correct for absolutely cavity-free crystals, when, as in this case, the results for the two methods only differ by 0.001, the author has finally accepted 2.666 as the density of potassium sulphate crystals at  $20^{\circ}$  compared with water at  $4^{\circ}$  taken as unity. It is highly satisfactory that this value is identical with that obtained by Retgers in the important work, which included the determination of the density of this salt, in which he employed for the first time the suspension method.

**Calculation of the Molecular Volume and Molecular Distance Ratios.**—Having thus settled the density of the crystals of the substance under investigation, we are in a position to calculate the molecular volume and the molecular distance (topic axial) ratios.

Molecular volume =  $\frac{\text{molecular weight}}{\text{density}}$ ; hence, to obtain the molecular volume we sum up the molecular weight from the atomic weights of the elements, multiplied in each case by the number of atoms of each present, and divide the result by the density found. In order to maintain the resulting molecular volumes for the different members of any related series, such as the isomorphous series of the alkali sulphates and selenates which has served us for so excellent an example, strictly comparable, all the densities, as we have seen, are determined for, or reduced to, the common standard temperature of  $20^{\circ}/4^{\circ}$ . Similarly, all molecular weights must be strictly comparable, and throughout his later published work the author has used the atomic weights authorised as most accurate by the International Committee on Atomic Weights in the year 1905, in which the atomic weight of hydrogen is taken as unity, brought up to date as regards all new determinations.

We will now complete the treatment of our example, potassium sulphate, by calculating its molecular volume, and its molecular distance ratios, using for the latter the formulæ shown in the last

chapter to apply to the series, on the most probable assumption of pseudo-hexagonal symmetry.

Molecular weight of  $K_2SO_4$ ,  $H = 1$ .

$$K_2 = 38.85 \times 2 = 77.70$$

$$S = 31.82$$

$$O_4 = 15.88 \times 4 = 63.52$$

---


$$\text{Mol. wt.} = 173.04.$$

$$\text{Molecular Volume of Potassium Sulphate} = \frac{173.04}{2.666} = 64.91.$$

*Molecular Distance Ratios of Potassium Sulphate.*—We have thus found that the volume  $V = 64.91$ , and it was shown in Chapter VIII. that the crystallographic axial values were  $a = 0.5727$ , and  $c = 0.7418$ . Inserting, therefore, these values in the formulæ we get :

$$\chi = \frac{1}{2} \sqrt{1 + a^2} \cdot \sqrt[3]{\frac{2V}{ac}} = 3.8810.$$

$$\psi = \sqrt[3]{\frac{2a^2V}{c}} = 3.8574; \quad \omega = \sqrt[3]{\frac{2c^2V}{a}} = 4.9964.$$

Thus the molecular distance ratios are :

$$\chi : \psi : \omega = 3.8810 : 3.8574 : 4.9964.$$

This chapter may fittingly end with a summary of the structural constants of the crystals of the whole isomorphous group of which potassium sulphate, which has been taken throughout as the most illuminating example which could be found of crystal structure, is the first member. The table will form a natural appendix to the comparative tables of the crystal angles and crystallographic axial ratios of the same orthorhombic group of salts, which were given in Chapter XXIV. (pages 382 and 383), and will serve as an example of how such a comparative table should be drawn up.

A further series of molecular distance ratios for these rhombic sulphates and selenates, calculated for the ordinary rectangular rhombic space-lattice No. 10 by the use of the formulæ given on page 591, will be found on page 703 in the next chapter (XXXIII.), in the discussion concerning the remarkable verification of the accuracy of the topic axial conception by the X-ray analysis of these salts.

The results indicated by the table on the following page are in full agreement with the important law stated on page 383, the molecular volumes and molecular distance ratios (topic axial ratios) being functions of the atomic weights or atomic numbers of the interchangeable alkali metals potassium, rubidium, and cæsium, elements belonging strictly to the same family group, in the cases of the crystals of the sulphates and selenates of those metals, which form an exclusive eutropic series within the isomorphous series. The thallium and ammonium salts (referring, of course, in the case of ammonium selenate to the rhombic variety only), while not



COMPARATIVE VALUES OF STRUCTURAL CONSTANTS OF ALKALI  
SULPHATES AND SELENATES.

Salt.	Density at 20°/4°.	Molecular Weight.	Molecular Volume.	Crystallographic Axial Ratios. <i>a</i> : <i>b</i> : <i>c</i> .	Topic Axial or Molecular Distance Ratios. <i>x</i> : <i>ψ</i> : <i>ω</i> .
K <sub>2</sub> SO <sub>4</sub> .	2.666	173.04	64.91	0.5727 : 1 : 0.7418	3.8810 : 3.8574 : 4.9964
Rb <sub>2</sub> SO <sub>4</sub> .	3.615	265.14	73.34	0.5723 : 1 : 0.7485	4.0304 : 4.0039 : 5.2366
Cs <sub>2</sub> SO <sub>4</sub> .	4.246	359.14	84.58	0.5712 : 1 : 0.7531	4.2187 : 4.1849 : 5.5175
Tl <sub>2</sub> SO <sub>4</sub> .	6.765	500.50	73.98	0.5555 : 1 : 0.7328	4.0820 : 3.9644 : 5.2299
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .	1.772	131.20	74.04	0.5635 : 1 : 0.7319	4.0792 : 4.0051 : 5.2020
K <sub>2</sub> SeO <sub>4</sub> .	3.067	219.82	71.67	0.5731 : 1 : 0.7319	4.0291 : 4.0068 : 5.1171
Rb <sub>2</sub> SeO <sub>4</sub> .	3.902	311.92	79.94	0.5708 : 1 : 0.7386	4.1672 : 4.1315 : 5.3461
Cs <sub>2</sub> SeO <sub>4</sub> .	4.456	405.92	91.09	0.5700 : 1 : 0.7424	4.3457 : 4.3040 : 5.6058
Tl <sub>2</sub> SeO <sub>4</sub> .	6.875	547.30	79.61	0.5551 : 1 : 0.7243	4.1124 : 4.0763 : 5.3189
(NH <sub>4</sub> ) <sub>2</sub> SeO <sub>4</sub> .	2.194	177.98	81.12	Not comparable	4.5939 : 4.2968 : 5.1506 <sup>1</sup>

belonging to the inner eutropic series, show constants nevertheless which entitle the crystals of those salts to be considered as belonging to the same isomorphous series, employing the term "isomorphous" in the sense which was defined on page 384 of Chapter XXIV.

Moreover, one very remarkable fact clearly shown in this table is worthy of special mention, as it has proved to have great significance. It is the close approximation of the molecular volumes and molecular distance ratios of rubidium and ammonium sulphates, indicating almost perfect iso-structure. It indicates that the replacement of two atoms of rubidium, Rb<sub>2</sub>, in Rb<sub>2</sub>SO<sub>4</sub> by two of the radicle ammonium groups, 2NH<sub>4</sub>, is accompanied by scarcely any appreciable change in the volume and dimensions of the unit-cell of the space-lattice of the crystal structure. This interesting fact is also observed throughout the monoclinic series of double sulphates and selenates crystallising with 6H<sub>2</sub>O, the rubidium and ammonium salts of any group (containing the same second metal) in all cases proving remarkably closely iso-structural.

The example afforded by this instructive series of salts will have emphasised in a striking manner the importance of the conception of molecular distance ratios, and have clearly demonstrated the enhanced value which now attaches to the accurate determination of the density of crystals. In fact, no crystallographic investigation can in future be considered complete which does not include such a determination, carried out with all the precautions described in this chapter.

<sup>1</sup> The molecular distance ratios of monoclinic ammonium selenate were calculated on the assumption of a similar pseudo-hexagonal structure to that of the nine rhombic salts. Such a structure is strikingly evident as regards the prism zone, the angles of the prism faces being 59° 38' and 30° 0', the prism zone thus resembling the well-known pseudo-hexagonal prism zone of the nine rhombic salts to a remarkable degree, considering the change of system.

## CHAPTER XXXIII

### X-RAYS AND CRYSTAL STRUCTURE—ABSOLUTE MEASUREMENT OF THE DIMENSIONS OF THE SPACE-LATTICE CELL—METHODS OF LAUE, BRAGG, AND DEBYE AND SCHERRER—THE LAW OF ATOMIC DIAMETERS

In the spring of the year 1912 the scientific world was considerably excited by the announcement that the X-rays, now so familiar to us from their use in surgery, and the nature of which is explained in Chapter XXXV., had been found to be capable of reflection from the various planes of atoms (those of the space-lattice) within crystals, and to afford after reflection or diffraction a direct indication on the usual fluorescent barium platino-cyanide screen, or indirectly after development on a sensitive photographic plate, in the form of a diagram of symmetrically arranged spots (a diffraction pattern), of the plan of symmetry on which the space-lattice of the crystal is constructed. The discovery was made by Dr. M. von Laue<sup>1</sup> in the physical laboratory of the University of Munich, with the assistance in the actual experiments of two collaborators, W. Friedrich and P. Knipping, and of the resources of the Mineralogical Department of Prof. von Groth. Dr. von Laue had been much struck by the fact that attempts which had then lately been made, by Haga and Wind, Walter and Pohl, and by Sommerfeld and Koch, to ascertain the approximate wave-length of X-rays, had all pointed to the neighbourhood of  $10^{-8}$  or  $10^{-9}$  centimetre, which is approximately the order of dimensions of atoms. He considered it most likely, therefore, that a crystal would behave towards X-rays as a three-dimensional grating, and that the constants of the grating would be mathematically connected in a simple manner with the directions along which the radiations diffracted from the atoms would reinforce one another. He suggested the experiment to his two collaborators, who at once tried it and found it to succeed perfectly. On a visit to Munich early in August of that year the author was shown the first photographs which had been taken with crystals of zinc blende. The discovery caused immense interest, and in a lecture delivered at the Royal Institution in November of the same year the author was enabled, by the kindness of Dr. von Laue, to exhibit on the screen transparencies of the original photographs, as well as a number of later ones, together with pictures of the apparatus used.

<sup>1</sup> M. von Laue, W. Friedrich, and P. Knipping, *Sitzungsber. der kais. Bayer. Akad.*, June 1912, 303 and 363.

The possibility of obtaining such remarkable photographs is thus due to the fact that the order of dimensions of chemical atoms and molecules on the one hand, and of the wave-lengths of X-rays on the other, is very similar. For instance, by the most recent developments of this research it has been shown that the lengths of the three different edges of the rectangular (orthorhombic) cells of the space-lattice of potassium sulphate (a cell which contains four molecules of  $\text{K}_2\text{SO}_4$ ) are  $5.731 \times 10^{-8}$ ,  $10.008 \times 10^{-8}$ , and  $7.424 \times 10^{-8}$  centimetre; while the wave-length of the X-radiation from a palladium anticathode which was employed in the measurements is  $0.584 \times 10^{-8}$  centimetre. Again the size (linear edge of cube) of an atom of hydrogen has been given (in the mean) by various observers as  $1.64 \times 10^{-8}$  centimetre, and its volume as  $1.64 \times 10^{-24}$  cubic centimetre (its mass being  $1.64 \times 10^{-24}$  gramme). The wave-length of X-rays is thus even somewhat smaller than the distances separating the atoms (or more correctly the centres of the atoms) in a crystal. On the other hand, a crystal acts as a continuous medium for light-waves, which are only of the order  $10^{-5}$  centimetre, no diffraction occurring owing to the smallness of the atoms compared with even the shortest wave-lengths of light (for violet light  $0.0004$  mm. =  $4 \times 10^{-5}$  cm.). The planes of atoms, the corners or nodes of the unit cells, of the crystal space-lattice thus act to the almost infinitesimally minute waves of the X-rays in a manner similar to that in which a diffraction grating acts towards the waves of light. The cases, while similar, are differentiated, however, by the fact that instead of a one-dimensional grating of ruled parallel lines we have in the case of the atomic space-lattice of a crystal a three-dimensional grating.

It will be shown in the discussion of the phenomena of diffraction in Chapter XXXVII., that the spectroscopic diffraction grating analyses a beam of white light into a spectrum of its component wave-trains by virtue of the system of parallel lines which are ruled (engraved) upon its surface at exactly equal intervals, several thousands to the inch, varying in number from 3000 (for projection purposes) to 20,000 (for use in spectroscopic investigation); a very suitable number for most research purposes is about 14,000 to the inch, for instance the Rowland gratings engraved on speculum metal with 14,438 lines to the inch, and their Thorpe replicas cast in celluloid and mounted on glass. When the beam of white light falls on such a grating, each line acts as a fresh centre from which a diffracted train of waves is radiated, and it is by the interaction and mutual interference of the similar trains from all the lines that the diffraction effects are due, namely, the spectra of the first, second, third, and higher orders which are produced. It will be shown that the conditions are expressed by the equation :

$$n\lambda = d \sin \theta,$$

in which  $n$  is the order of the spectrum,  $\lambda$  the wave-length of the light,  $d$  the distance between the centres of adjacent lines, and  $\theta$  the angle of diffraction for normal incidence.

**The Laue Radiograms.**—Laue's discovery has been the means of proving the Röntgen X-radiations to be transverse electromagnetic wave-move-



ments resembling those of light, and of enabling their very much shorter wave-lengths to be determined with accuracy; at the same time it has provided direct experimental proof of the correctness of the views of crystallographers, put forward in both the first and the present editions of this book, that the basis of crystal structure is a space-lattice arrangement of the atoms, and that the regular interpenetration of space-lattices formed by the atoms of the same chemical element produces even the more complicated crystalline structure of chemical compounds.

FIG. 530.—Early Laue X-radiogram of Zinc Blende.

A reproduction of two of these historically interesting first X-ray photographs, afforded by a crystal of zinc blende, is given in Figs. 530 and 531, in both of which the incident rays were perpendicular to a cube face; but for Fig. 531 the photographic plate was twice as far from the crystal as for Fig. 530. The apparatus with which they were taken is shown in Fig. 532, which is a repro-

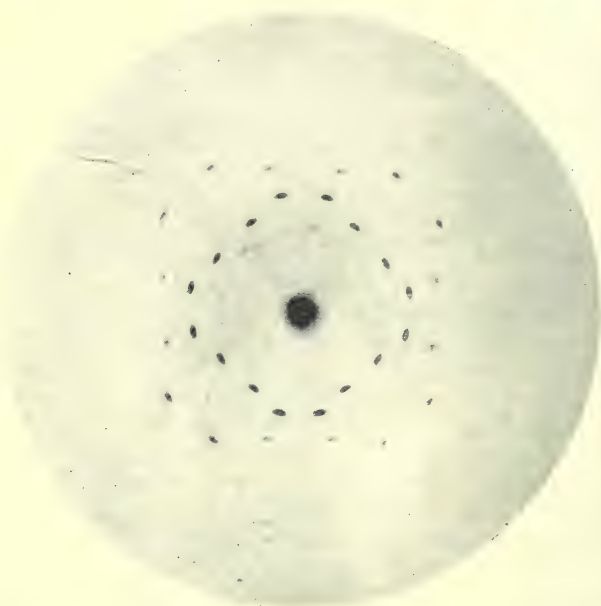


FIG. 531.—Laue X-radiogram of Zinc Blende, perpendicular to a Cube Face.

duction of the transparency received from Dr. Laue in 1912. A diagram by Dr. Laue, illustrating the arrangement, is also given in Fig. 533.

X-rays from a Crookes tube actuated by an induction coil were passed through small apertures in a succession of leaden screens  $B_1$ ,  $B_2$ ,  $B_3$ ,  $B_4$  (lead being impervious to X-rays),  $B_4$  being a plate of lead one centimetre thick, pierced by a cylindrical hole 0.75 millimetre in diameter; the very

fine beam thus obtained was then received normally on the cube face of the crystal Kr of zinc blende. The crystal was supported on a goniometer G, and adjusted so that the face in question was exactly perpendicular to the axis of the fine boring in the last leaden screen. A short distance

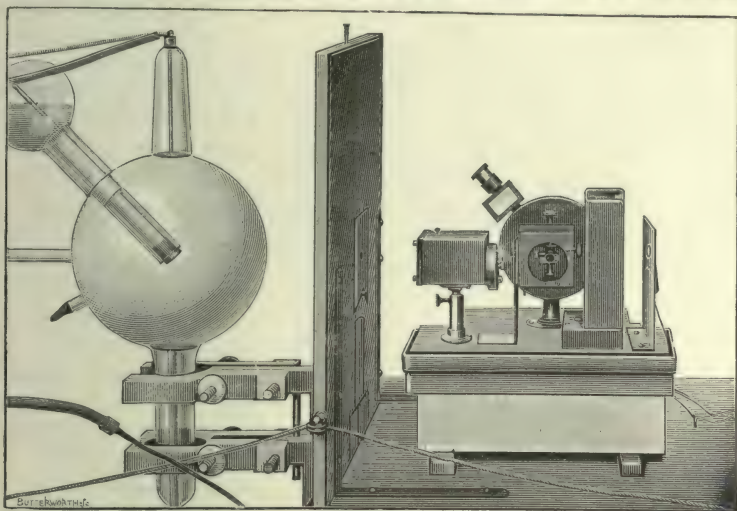


FIG. 532.—Laue's Original Apparatus for Crystal X-radiograms.

behind the crystal a photographic plate  $P_4$  was supported in such a manner as to receive at its centre the directly transmitted beam of X-rays, and around this central spot (by far the darkest and largest shown on the plate) the various deflected rays, the reflections or diffractions from the variously orientated planes of atoms of the space-lattice, were arranged, and corresponding smaller spots due to them revealed on development. Other sensitive plates  $P_1$  to  $P_5$  were also placed at different positions around the beam. The pattern of both the spot diagrams reproduced in Figs. 530 and 531 obviously exhibits very clearly the symmetry of the cubic system to which zinc blende belongs. A typical crystal of zinc blende is shown in Fig. 113 on page 162. The specimen of zinc blende used at Munich was a plate 1 centimetre square, cut from a very good crystal, parallel to a cube face. The photographs show well the symmetry of the spots about the tetragonal axis of symmetry perpendicular to the plate. A third spot photograph is also

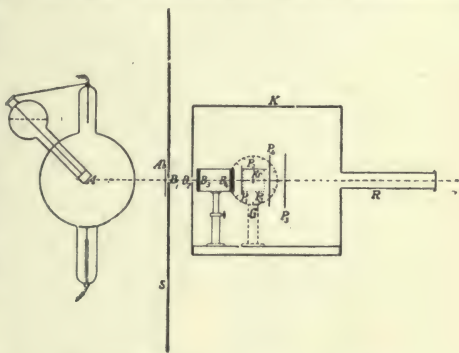


FIG. 533.—Diagram of Laue's Apparatus.

reproduced in Fig. 534, for which the incident rays were perpendicular to an octahedron face (really a tetrahedron face, zinc blende belonging to



FIG. 534.—X-radiogram of Zinc Blende perpendicular to an Octahedron Face.

class 31), and parallel to one of the trigonal axes of symmetry of the cubic system; it exhibits the trigonal symmetry admirably. In Fig. 535, also reproduced from one of Laue's photographs, the spot diagram afforded by a quartz crystal (a plate cut perpendicular to the axis) is given, showing clearly the symmetry of the trigonal system.

An improved installation for producing the Laue radiograms in a more accurate manner has been described by Wulff,<sup>1</sup> and is constructed by Fuess. It is illustrated in Fig. 536 in a diagrammatic form

taken from Wulff's memoir. It enables more accurate adjustments of all the parts of the apparatus, including the photographic plates, and careful measurements of their relative positions, to be made.

The centre of the arrangement is a Czapski theodolite goniometer (see page 451, Fig. 365) G, which proves particularly suitable for this work. Its telescope replaces the cathetometer used by Friedrich and Knipping. The whole apparatus is enclosed in a chamber with two compartments K and K' which are lined inside with sheet lead, one K for the Crookes-Röntgen tube R and the other K' for the goniometer G. The first compartment K is provided with a door on the right, for the manipulation of the X-ray tube

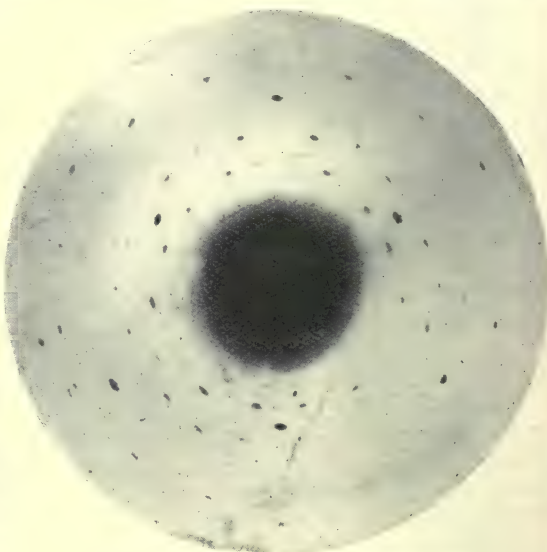


FIG. 535.—X-radiogram of Quartz with Plate perpendicular to the Axis.

<sup>1</sup> *Zeitschr. für Kryst.*, 1914, 54, 59.



and electrical arrangements; it has a lead-glass window, for observation of the tube and its proper illumination. The roof of this compartment is also provided with an opening with removable cover, for ventilation purposes. The electrodes pass into the compartment through two ebonite cylinders  $E_1$  and  $E_2$ . The tube is supported on an adjustable stand  $SS$ , so that the focus of the anticathode  $A$  can be brought into the straight line which passes through the openings  $d_1$  and  $d_2$  between  $K$  and  $K'$  and the crystal  $k$ . In the same compartment  $K$  there is also an electric glow-lamp  $L$ , arranged on a lever so that it can be brought into position for ordinary illumination of the crystal during adjusting operations, or removed out of the way when the X-ray tube is at work. The two circular diaphragm openings

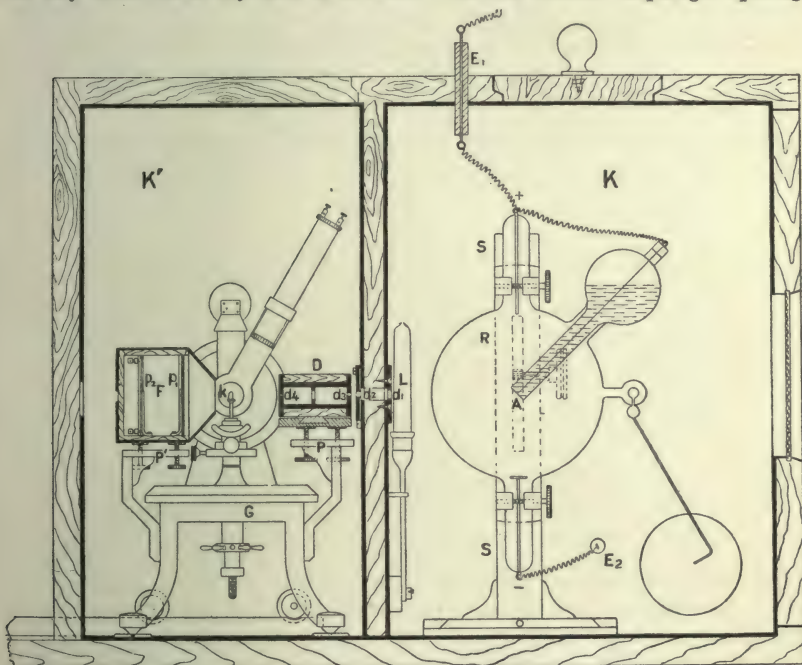


FIG. 536.—Fuess Installation for Production of X-radiograms.

$d_1$  and  $d_2$  between  $K$  and  $K'$  are bored through the leaden plates, and also have adjustable covering plates of lead with more constricted apertures of graduated sizes; the largest,  $d_1$ , is a hole of 1 cm. diameter, and  $d_2$  is of 0.5 cm. diameter. There are also two further apertures in still thicker plates of lead,  $d_3$  and  $d_4$ , graduated in size still smaller and smaller, the last aperture,  $d_4$ , giving the final form to the beam of X-rays. The diaphragms  $d_3$  and  $d_4$  are supported at the ends of a wide tube  $D$ , which is carried in an adjustable manner on a plate  $P$  carried on an arm fixed to the basal stand of the goniometer  $G$ . On a similar opposite arm of the latter a similar plate  $P'$  is arranged to carry, also with adjustments, the photographic plate-box  $F$ , which is arranged for two sensitive plates,  $p_1$  and  $p_2$ , 5 cm. apart.

Full directions for the use of the apparatus are given in the memoir.

**A Crystal as a Three-dimensional Grating for X-rays.**—Considering now the case of a crystal as a three-dimensional grating, let  $pppp$  in Fig. 537 represent four parallel rows of atoms, spaced at equal distances  $d$  apart,

and  $A, A_1, A_2, A_3$  represent a train of advancing X-ray waves meeting the planes of atoms obliquely, and  $BC$  be the reflected ray at the point of contact  $B$  with the first plane of atoms. Other rays, however, reflected from the second, third, and fourth planes of atoms also join in moving along  $BC$ , and if we consider the distances which they must travel from the original plane wave-front  $A A' A'' A'''$  in order to reach  $C$  we have the following facts. The paths are respectively  $ABC, A'B'C, A''B''C, A'''B'''C$ , etc. If we produce  $A'B'$  to  $D$ , and draw  $BN$  perpendicular to  $B'D$ , we see that as  $B'D = B'B$  (the angles at  $B$  and  $D$  of the triangle  $BB'D$  being equal, namely, the complement of the glancing angle  $\theta$ , in accordance with the law of reflection), and  $A'N = AB$ , the difference of path between  $A'B'C$  and  $ABC$  is equal to  $ND$ . Now  $\frac{ND}{BD} = \sin \theta$  and  $BD = 2d$ ; hence  $ND$  is equal to  $2d \sin \theta$ . Similarly,  $A''B''C$  is greater than  $A'B'C$ , and  $A'''B'''C$  than  $A''B''C$ , by the same distance  $2d \sin \theta$ . If  $ND$  be the

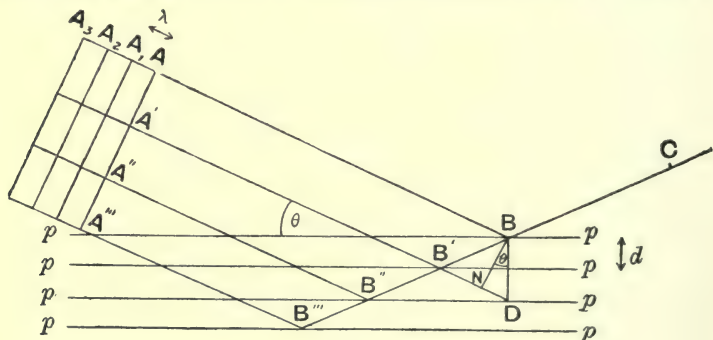


FIG. 537.

actual length of the wave (when we have  $\lambda = 2d \sin \theta$ ), or an exact multiple of the wave-length, all the wave-trains reflected by the planes of atoms  $pppp$ , etc., will be in the same phase, and will reinforce one another, their amplitudes being added together. If, however, it vary even slightly from this the innumerable phase differences are found in practice to destroy one another. Hence, when a "monochromatic" wave-train of X-rays of wave-length  $\lambda$  is allowed to strike the crystal, clear reflection is only observed to occur when the glancing angle<sup>1</sup> of diffraction has certain definite values,  $\theta_1, \theta_2, \theta_3$ , etc., which are afforded by the equations:

$$\lambda = 2d \sin \theta_1, \quad 2\lambda = 2d \sin \theta_2, \quad 3\lambda = 2d \sin \theta_3, \text{ etc.}$$

The angles  $\theta_1, \theta_2, \theta_3$ , etc., are obviously those the sines of which are rational multiples of each other, the value of the right-hand side of the equation being thus doubled, tripled, etc., in accordance and equality with the doubling, tripling, etc., of the wave-length on the left-hand side of the equation.

The reflection at  $\theta_1$  is termed that of the first order, that at  $\theta_2$  is

<sup>1</sup> By "glancing" angle is meant the angle with the reflecting plane, and not the complementary "angle of incidence," which, according to the usual convention, is that made with the normal to the plane.

said to be of the second order, and  $\theta_3$  corresponds to the third order. As the crystal is rotated, therefore, with the beam of X-rays impinging on the face chosen for the experiment at gradually varying angles, strong reflection is observed at certain positions, corresponding to these glancing angles  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$ , etc., of reflection from the planes of atoms parallel to the face, while between these positions practically no reflection is observed. The crystal thus requires to be adjusted to exactly the right (correct) angle, and then only affords the spectrum of one order at a time; the three-dimensional crystal grating is thus very different in its action to the ordinary line grating, which affords several orders of spectra at once, and at any effective angle.

If now another face be proceeded to, corresponding to a different spacing  $d'$  of the planes of atoms to which it is parallel, a similar result is obtained, but at a different series of angles  $\theta'_1$ ,  $\theta'_2$ ,  $\theta'_3$ , etc., and for this case:

$$\lambda = 2d' \sin \theta'_1, \quad 2\lambda = 2d' \sin \theta'_2, \quad 3\lambda = 2d' \sin \theta'_3, \text{ etc.}$$

It is only necessary carefully to measure the glancing angle  $\theta$  or  $\theta'$ , in order to obtain the relation between the wave-length  $\lambda$  of the X-radiation employed and the spacing  $d$  or  $d'$  of the planes of atoms of the crystal space-lattice, assuming that the correct order of the spectrum be recognised, and that the wave-length of the X-radiation be accurately known, as is the case for the palladium and rhodium anticathode rays which are largely employed; the absolute dimensions of the spacing are then afforded directly.

It cannot be made too clear that it is not surface reflection of X-rays on an exterior crystal face which is occurring. No such surface reflection of X-rays is possible to the extent observed, for the first few layers combined are incapable of diffracting any appreciable proportion of the rays; the latter have to pass through millions of layers before the X-rays are appreciably absorbed. It has, in fact, been definitely proved in the cases of quartz and gypsum, by roughening the surfaces of the crystal faces, that the surface layers are not appreciably concerned. For the intensity of the X-ray reflection was scarcely, if at all, diminished by such treatment. The combined effect of a very large number of successive parallel planes of atoms is, however, sufficient to afford diffracted or reflected rays of intensity adequate to produce the observed effect on the photographic plate. The effective plane has been defined by F. C. Blake<sup>1</sup> as that plane at which, if reflection for all the X-rays occurred at that plane only, the effect would be the same as that which is actually produced, due to the different reflections from all the planes of atoms playing any part. For calcite the effective plane has been found to be at a depth of 0.202 mm.

#### The Bragg Method of Spectrometric X-ray Analysis of Crystal Structure.

—We are indebted for the great progress which has been made in this subject, since the inception of the photographic method of X-ray crystal

<sup>1</sup> *Nat. Acad. Sci. Proc.*, 1918, 4, 236.



radiography by Laue, to Sir William H. Bragg<sup>1</sup> and his son Prof. W. L. Bragg, to whom the discussion of the conditions just laid down are due. Their chief contribution, however, has been the introduction of a new method of attack, involving the use of the principles just discussed, but with a new kind of receiving apparatus, that of the X-ray spectrometer, instead of the photographic method. It depends essentially on the use of a homogeneous (monochromatic) X-radiation, and the measurement by a form of spectrometer of the glancing angles of reflection and the intensity of the reflection. Before describing this new procedure, however, it may be mentioned at once, in order to complete the discussion of the conditions as given in the above equations, that the Braggs have determined with great accuracy the wave-lengths ( $\lambda$  in the equations) of an adequate number of "monochromatic" X-radiations, or "lines" of definite wave-length in the X-ray spectra of certain metals. This was accomplished by the use of crystals of which by their method they had already determined with great certainty the constitution, so that they have been able to employ the equations of the form  $n\lambda = 2d \sin \theta$  in the determination of the spacing and atomic distribution in the crystals of many other substances. For instance, an X-radiation which has proved to be of the greatest possible value is that already referred to from a palladium anticathode. Its wave-length was found to be  $0.584 \times 10^{-8}$  centimetre, from the fact that the planes of atoms parallel to a cube face of a crystal of rock-salt, NaCl, are spaced at intervals of  $2.81 \times 10^{-8}$  (as determined by numerous experiments with X-rays of many different wave-lengths), and that they afford strong reflections of the palladium rays at the angles  $5.9^\circ$  (first order reflection),  $11.85^\circ$  (second order reflection), and  $18.15^\circ$  (third order reflection). Using the equation  $n\lambda = 2d \sin \theta$ , we have for the first order  $\lambda = 2 \times 2.81 \times 10^{-8} \sin 5.9^\circ$ , for instance, and obtain the value  $0.584 \times 10^{-8}$  centimetre for the wave-length of the palladium X-radiation.

In the case of Laue's direct transmission photographs the same numerical considerations apply. But in this case not only do the planes of atoms normal to the incident rays and parallel to the crystal face come into play, but also other planes of the same atoms; for the space-lattice affords as many such planes of atoms as there are simple facial planes developed or possible. From each of these planes diffraction spot-reflections are afforded, arranged around the central spot of the directly transmitted incident ray in accordance with their symmetry. In general the reflections become feebler as the complexity of the plane (and of its corresponding facial indices) increases, so that the spot diagram is chiefly a record of the position of the simpler and more fundamental planes, and also principally of the first order reflections. For "white" X-radiations (that is, of all wave-lengths produced by the bulb) are employed. Some of the most recent radiograms, however, notably those prepared by Jaeger and by Rinne, have exhibited an enormous number of spots, corresponding to a very large number of possible facial forms, the clearness and definition being truly remarkable (see pages 706 and 707).

<sup>1</sup> *X-Rays and Crystal Structure*, by W. H. and W. L. Bragg (G. Bell & Sons, 1916).

According to Jaeger, each spot would be differently "coloured" in the spot radiogram, if X-rays were visible like light rays, owing to the fact that "white" X-radiations involving many wave-lengths are employed.

The Bragg method enables us to go much further than this, namely, by using "monochromatic" (definite wave-length) X-radiations, to obtain definite records of the second and third order reflections also, that is, for each set of planes of atoms, to determine the few special angles at which alone reflection can now occur in accordance with the equation  $n\lambda = 2d \sin \theta$ ; and it is by the aid largely of this additional information,

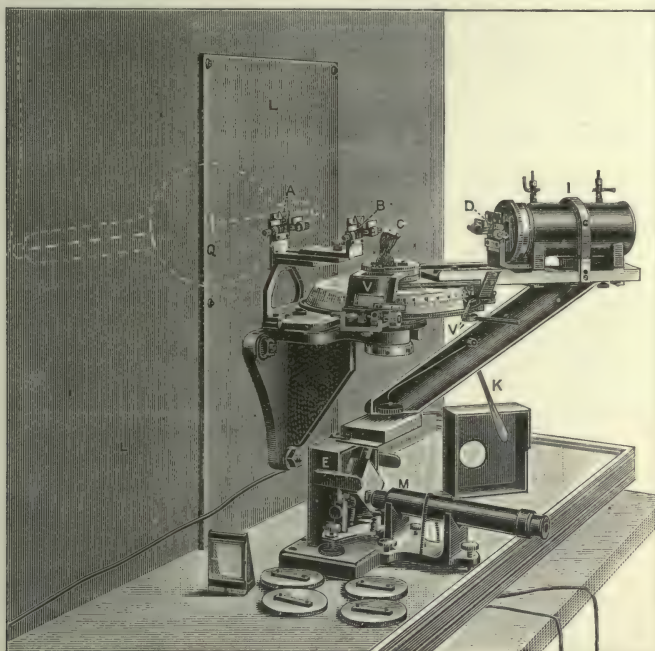


FIG. 538.—The Bragg X-ray Spectrometer.

especially from the relative intensities of the various orders of X-ray spectra, that it has become possible not only to elucidate the dimensions and shape of the elementary cell of the space-lattice, but to determine how many, if more than one, chemical molecules are included in the cell (that is, how many molecules are to be associated with each point of the space-lattice), and to fix the exact location of the numerous atoms of the different elements which are included in those molecules and in the whole space-lattice cell.

Sir William Bragg's apparatus consists of an ordinary spectrometer adapted for use with X-rays, in which the usual telescope is replaced by a similar-looking but wider tube, filled with sulphur dioxide gas or methyl bromide vapour, which acts as an ionisation chamber; this affords a very

delicate test, in conjunction with a sensitive electroscope, for the position of the reflections corresponding to the glancing angles, enabling the feebler second and third order reflections to be detected, such as would not register themselves at all, or only very faintly, by the Laue photographic method.

The apparatus is shown in Fig. 538, as in actual use in Sir William Bragg's laboratory at University College, London, in 1921. The ionisation chamber of the X-ray spectrometer is the wide brass tube I, 15 cm. long and 5 cm. in diameter, which is

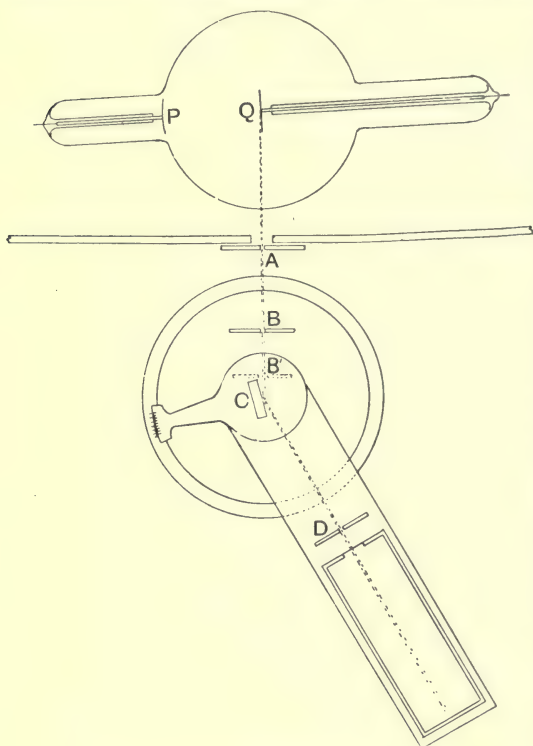


FIG. 539.—Diagram of X-ray Spectrometer.

rotatable about the same fixed axis as the crystal C; the latter (when large, as shown) is mounted in the centre of the goniometer, at the summit of a cone (conveniently deformed to support the crystal rigidly) of goniometer wax, built up on the usual spectrometer adjusting table, as shown in Fig. 538. This latter may, when desirable (the crystal being small), be replaced by goniometrical centring and adjusting movements carrying the crystal on a small wax cone at their summit. The little rotating table which thus carries the crystal moves over the fixed divided circle and is provided with the vernier V. The ionisation chamber is also independently provided with an arm carrying a vernier V', likewise moving over the divided circle; and it carries an adjustable slit D at its entrance. A and B are other slits in leaden screens, and

L is a leaden box behind which the X-ray bulb is sheltered, as shown outlined in white broken lines (although not quite in the adjusted position for actual use). The general mode of arrangement will perhaps be better understood with the aid of Fig. 539.

The electroscope E is one of the Wilson tilted type, the movable gold leaf of which indicates the ionisation effect, the movement of the leaf being observed and measured by the microscope M; the electroscope is thoroughly well electrically shielded, and the outer shield is provided with an earthing key. The X-ray tube is usually run in a steady and very "soft" state (that is, the vacuum is only moderately high, electrons are plentiful and slow, and the X-rays are not very penetrating). A special form of X-ray bulb (Crookes tube) in which the anticathode Q is perpendicular to the stream of cathode rays is specially convenient, an idea due to Prof. R. W. Wood.



The pencil of rays then leaves the anticathode at a grazing angle, as shown in Fig. 539, the centre of the pencil passes exactly through the axis of the spectrometer, and the evil effect of any wandering of the cathode spot over the surface of an inclined anticathode is avoided. Each metal used as anticathode is stimulated by the cathode rays to emit its own characteristic X-rays, the most intensive "lines" being usually those of either the well-known K or L series. Platinum, palladium, rhodium, and tungsten have proved the most suitable metals for anticathodes. Platinum affords three principal lines of the respective wave-lengths  $1.316 \times 10^{-8}$  cm.,  $1.104 \times 10^{-8}$  cm., and  $0.960 \times 10^{-8}$  cm. Palladium gives two of wave-lengths  $0.584 \times 10^{-8}$  cm. and (less intense)  $0.509 \times 10^{-8}$  cm. Rhodium emits four, of the wave-lengths 0.537, 0.545, 0.614, and  $0.619 \times 10^{-8}$  cm. Tungsten affords a single intense line, of the wave-length  $1.486 \times 10^{-8}$  cm.

The ionisation chamber is usually filled with sulphur dioxide, but when the more penetrating X-rays (from a bulb worked "hard," at high vacuum) are employed methyl bromide is substituted with advantage. Both these vapours yield a relatively large ionisation current (ten times that afforded by air). The chamber is insulated and raised to a high potential by a battery of storage cells, the electrode being inside the chamber, and a fine wire leads from it to the electroscope, through a sulphur plug. A key K connects the electrode with earth, and when it is raised, and the X-rays are turned on and the crystal is in position at the glancing angle, the ionisation current flows into the electroscope, and the deflection of the gold leaf is read off by the microscope, a strong reflection from the crystal causing the leaf to move at the rate of ten or twenty scale divisions per second.

The ionisation of gases by X-rays is effected by the electrons ( $\beta$ -rays) which spring up in their path, derived chiefly from the walls of the chamber unless the gas be very dense, and to which their energy is transferred. The electrons immediately form electrically charged (both + and -) molecules in the gas, each electron attaching to itself a number of molecules. These gas "ions" impart conductivity to the gas, and the charged condition persists until the mutual neutralisation of the + and - ions is accomplished. It lasts quite long enough to affect a Wilson gold-leaf tilted electroscope.

Prof. W. L. Bragg has employed in his later work at Manchester University with the X-ray spectrometer a Lutz-Edelmann (Munich) "string electrometer" as electroscope, as illustrated in Fig. 539a. Its advantages are small capacity and large range of sensitivity. The "string" is of quartz fibre, silvered to render it conducting; it is attached at both ends, so that it is the "sag" which is observed, as a

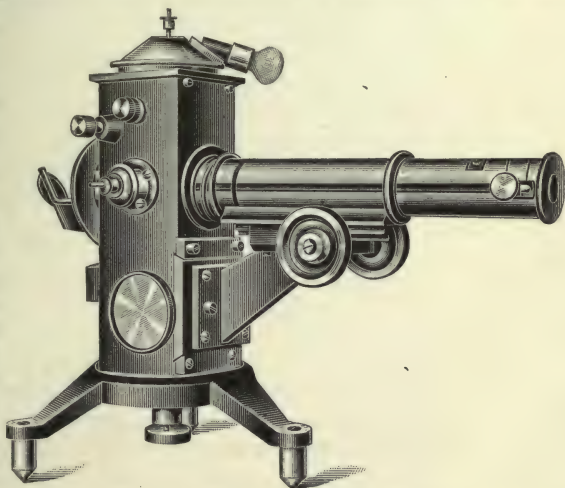


FIG. 539a.—The Lutz-Edelmann Electrometer.

vertical line crossing the field of the microscope. A null method of measuring the charge received from the ionisation chamber is adopted. A small cylindrical condenser is placed in parallel with it, the inner plate being connected to the

electrometer and the outer plate to a potentiometer. When a charge is received the string is displaced to one side, and is brought back to its zero by charging the outer plate to a measured potential by means of the potentiometer, so as to induce a charge on the inner plate adequate just to neutralise that received from the ionisation chamber.

In certain experiments, such as the mapping of the X-ray spectra, the ionisation chamber may be replaced by a photographic plate as sensitive receiver and indicator of the reflected X-rays and their intensity. An apparatus has been constructed for Sir William Bragg by Messrs. Hilger provided with an adjustable carrier for a photographic plate, and also with a means of rotating the crystal through a greater or less arc with a rapid reciprocating motion. The crystal is mounted at the centre of a large ring, carried on the adjusting movements above the circle, so that any face can be brought vertical, so as to reflect the X-rays to the plate either while still or during its rapid motion. A somewhat similar apparatus is described by C. D. Cooksey,<sup>1</sup> which has been used for accurate determinations of X-ray wave-lengths. For the analysis of crystal structure, however, the ionisation chamber is far the best.

The essence of the X-ray spectrometric method is, therefore, that the various glancing angles  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$ , etc., at which a plane of atoms serves as an efficient reflector, are determined, and the results interpreted in accordance with the equation  $n\lambda = 2d \sin \theta$ .

As with the diffraction grating, in ordinary circumstances the intensity of the reflected radiations diminishes as the order increases. There are, however, exceptions to this, when successive planes of atoms differ in composition or in their distances of separation; even orders may then become stronger than odd ones and certain orders may not be detectable at all. For instance, in the case of sodium chloride (rock-salt) the cube planes afford reflections of a regular type, the first order reflection being by far the strongest, then the second order not so strong, and subsequently a relatively weak third order reflection, indicating the fact, now well confirmed, that successive cube planes are identical in every respect. The general average of the intensities of the 1st, 2nd, 3rd, 4th, and 5th order spectra, for planes uniform and uniformly spaced, were at first supposed to be respectively 100 : 20 : 7 : 3 : 1; but later Sir William Bragg assumes the intensities to be as the inverse squares of the orders. This average is well conformed to by the cube planes of rock-salt. On the other hand, the reflections from the octahedral planes of atoms of rock-salt show a weak first order, a strong second order, a very feeble third order, and a somewhat stronger fourth order reflection, in conformity with the fact that the octahedral planes are alternately those of sodium and of chlorine atoms. In order further to elucidate this point it will now be best to pass to the consideration of rock-salt in more detail, as an example of the Bragg method and results.

**Rock-salt.**—The structure of sodium chloride crystals, NaCl, as revealed

<sup>1</sup> *Phys. Rev.*, 1920, 16, 305.

by the X-rays, is shown in Fig. 540, the solid dots representing either the metal or the halogen and the ring-dots *vice versa*. In either case the structure, considering one kind of atoms alone, is that of the face-centred cubic space-lattice No. 3 (see page 583) shown in Fig. 541. The planes of atoms parallel to the cube faces  $\{100\}$  are obviously all identically similar and composed of equal numbers of sodium and chlorine atoms; but the planes of atoms parallel to the octahedral faces  $\{111\}$  are composed

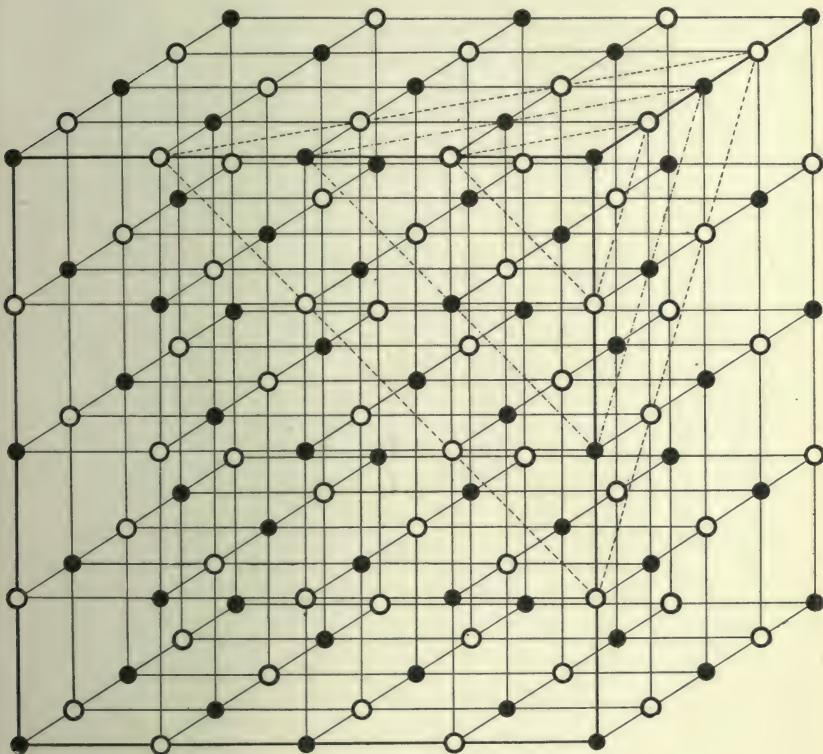


FIG. 540.—The Structure of Rock-salt.

of either one element or the other, the two varieties of planes being arranged regularly alternately. Indeed the structure of rock-salt may be regarded as composed of two interpenetrating face-centred cube lattices, the sodium atoms on one and the chlorine atoms on the other, the two being relatively situated as shown in Fig. 540. The distance between any pair of atoms (a sodium atom and a chlorine atom) on any of the rectangular lines in the figure, that is, half the length of the side of the whole large cube or the full size of the edge of one of the small cubes, is  $2.81 \times 10^{-8}$  centimetre.

There is, however, also another principle at work, for Sir William



Bragg has discovered that the intensity of reflection from an atom, that is, the efficiency of an atom as a scatterer of X-rays, is proportional to its atomic weight (regarding the latter as a measure of mass).<sup>1</sup> In the case of sodium chloride we are dealing with atoms of atomic weights 23 and 35.5 respectively. The successive octahedral planes reflect consequently with alternating efficiency in this proportion; it is only the alternate identically similar planes that correspond to the  $d$  in the equation

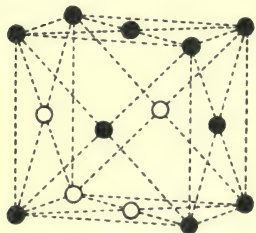


FIG. 541.—The Face-centred Cubic Space-lattice.

$\lambda = 2d_{(111)} \sin \theta$ . Owing to the difference in atomic weight and atomic number of the atoms in the two alternating sets of planes, those of sodium and those of chlorine, the first order reflections are not exactly balanced and thus do not quite extinguish each other, so that there is some first order reflection observed; but its intensity is much less than that of the second order reflection, for which there is a considerable balance of reinforcement effect. We thus obtain a weak first order and much weaker third order reflection, a strong second order, and also quite a good fourth order reflection from the octahedral planes of atoms of rock-salt. These facts are more fully explained on page 659.

An analogy with a ruled-line diffraction grating would be effected if every alternate line were ruled a little wider than the others, so that it diffracted more light. A spectrum would then appear corresponding to the distance  $2d$  between the widened lines, and instead of the equation  $n\lambda = d \sin \theta$  we should have the conditions represented by  $n\lambda = 2d \sin \theta$ .

**Potassium Chloride.**—The case of the analogous chloride of potassium, KCl, is very instructive. For here the atoms of potassium and chlorine are of nearly equal atomic weight, namely 39.1 and 35.5. They are so close in this respect that when the octahedral planes of atoms are adjusted the spectra of odd order are almost absolutely cut out, and all the points, whether solid or ring-dots, in Fig. 540 are of practically equal value. Moreover, this converts the space-lattice into one of the simple-cube variety No. 1 (page 583). That is, the crystal behaves as if the  $d_{(111)}$  in the equation  $\lambda = 2d_{(111)} \sin \theta$  were the distance between a potassium octahedral plane and the next chlorine octahedral plane of atoms. The spacings, in fact, of the cube planes {100}, of the rhombic dodecahedral planes {110}, and of the octahedral planes {111} are apparently those of a simple-cubic lattice, No. 1.

**Interpretation of Intensity of X-ray Spectra.**—This matter of the intensities of the different orders of X-ray reflection from atomic planes in crystals, and their relation to the nature of those planes, that is,

<sup>1</sup> It is more probably accurate to say "atomic number" rather than "atomic weight"; for the amplitude is proportional to the number of electrons per unit area, which Moseley has shown is the same number as the atomic number (sequence number of the element in the periodic table), rather than to the gravitational mass. Atomic weight, however, varies approximately proportionally to the atomic number.

whether they are composed of atoms of the same elements (or elements of similar, nearly equal, mass), or of different elements of appreciably different mass as represented by their atomic weights and atomic numbers, is one of the greatest importance. It is hoped that the following additional statement concerning it, which has been drawn up after consultation with Sir William Bragg, will render it clear.

We start, as already laid down, with the fundamental equations for the successive orders of reflection :

$$\begin{aligned}\lambda &= 2d \sin \theta_1, \\ 2\lambda &= 2d \sin \theta_2, \\ 3\lambda &= 2d \sin \theta_3, \text{ etc.}\end{aligned}$$

The sines of  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$ , etc., are as 1, 2, 3, etc. For instance, in a particular experiment with rock-salt, using a palladium anticathode, reflections were obtained from (100) cube planes at  $5.9^\circ$ ,  $11.85^\circ$ ,  $18.15^\circ$ , etc., and the sines of these angles are as 1 : 2 : 3 almost exactly, indicating that they correspond to first, second, and third order spectra respectively. In other words, the equation always remaining an equation, when we multiply the wave-length of the X-radiation on the left by an integer we similarly multiply the right-hand side by multiplying the sine of the angle of reflection of the X-rays, the angle itself being thus increased (counting from the plane of the crystal face, the glancing plane, and not from the normal to the face and plane of atoms). Hence, we may state :

1. The effect of getting reinforcement and therefore brilliant reflection at double or triple wave-length distances, represented in the equation by the doubling or tripling (or further multiplying) of the wave-length of the X-radiation, the spacing remaining the same, is to get the reflection at a larger glancing angle  $\theta_2$ ,  $\theta_3$ , etc., namely, one the sine of which is twice or three times (or more) as much as  $\sin \theta_1$ .

But the right-hand side of the equation can also be doubled, trebled, etc., by multiplying  $d$  instead of the sine ; when we do so by 2, keeping the glancing angle and therefore its sine the same, the second order reflection produced by double wave-lengths  $2\lambda$  corresponds obviously to this double spacing  $2d$ , which we may call  $D$  (that is,  $D = 2d$ ). Similarly,  $3\lambda$  would correspond to a spacing  $= 3d$ , and the reflection is a third order one. But there will, of course, be now a new first order reflection, at a smaller angle, such that its sine is half of that of the angle corresponding to  $D = 2d$ . Hence, we may make a second statement as follows :

2. If we double the spacing  $d$ , calling it  $D$  (equal to  $2d$ ), which is equivalent to getting reflections from alternate planes only, we have for the first order reflection  $\lambda = 2D \sin \theta'$ . In order that the right-hand side shall really remain the same, equal to the wave-length, as the spacing is now doubled, namely  $D = 2d$  instead of  $d$ , the value of  $\sin \theta'$  must be only half as much as that of  $\sin \theta_1$ , that is,  $\sin \theta' = \frac{\sin \theta_1}{2}$ . This comes to

the same thing as considering  $\theta_1$  as the second order reflection angle, and we may indeed call it the  $\theta_2$  for this double spacing,  $\theta'$  being really the  $\theta_1$  for this spacing. In other words, for the spacing  $D (= 2d)$  the glancing

angle corresponding to the first order reflection is smaller than the first order glancing angle for the spacing  $d$ , by an amount which corresponds to the relations of the sines of the two angles being as 1 (for  $D$ ) to 2 (for  $d$ ).

If we now go back to the spacing  $d$ , we can get this from the spacing  $D (=2d)$  just considered by introducing planes of similar (same element)

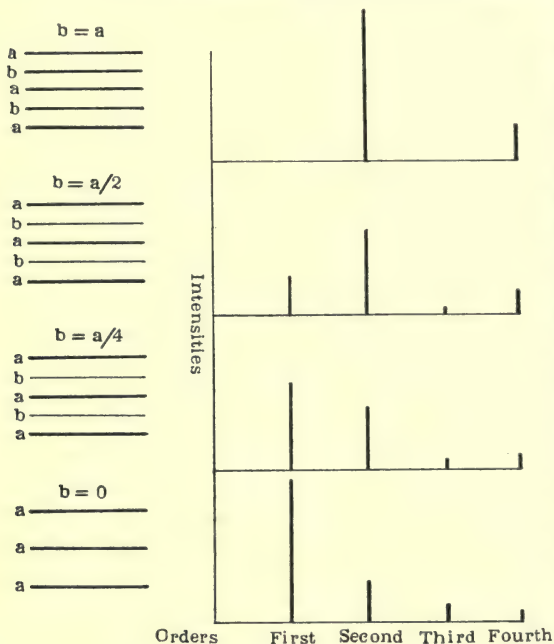


FIG. 541a.—Relation between Densities of Alternate Planes of Atoms and Intensities of Reflection Orders.

$D$ , and planes of different atoms (those of another element) interspersed midway between them, so that adjacent planes irrespective of composition are spaced at the distance  $d$  (where  $2d = D$ ), we shall have a differential effect occurring, dependent on the similarity or difference of the atomic weights and atomic numbers (as representing the relative masses of the atoms) of the two elements of which the two kinds of atomic planes are composed.

These vitally important facts are illustrated and rendered very clear by the diagram given in Fig. 541a, which, together with the next statement 4, has been directly suggested by Sir William Bragg to the author. The bottom row of spectra in the diagram and their intensities correspond to the spacing  $D = 2d$ , and the top one refers to the spacing  $d$ .

4. "Consider the effect of a set of parallel atom-bearing planes uniformly spaced but alternately of unequal densities  $a$  and  $b$ . The accompanying diagram (Fig. 541a) shows the effect of giving  $b$  various values, beginning with  $a$  and ending in zero. The relative intensities of the

atoms half-way between the  $D$  planes. The reflections from one set of alternate planes, 1, 3, 5, 7, etc., will then be contrary in phase to the other alternate set, 2, 4, 6, 8, etc., and the reflections will be mutually extinguished, namely, those corresponding to  $D$ . But we shall now get reflections corresponding to the spacing  $d$ . Supposing, however, that the intermediate planes introduced are not composed of atoms of the same element as the  $D$  planes, we have the following very interesting case:

3. When we have planes of similar atoms spaced at the distance



different orders are shown in each case. It is assumed that when the planes are all alike and equally spaced the intensities in the different orders are as the inverse squares of the orders, because some assumption is necessary for the purpose of illustration and this particular assumption has been found to be nearly correct in several cases."

When the planes are alternately composed of different elements (like the octahedral sodium and chlorine planes of rock-salt, NaCl), we are really getting some reflection at this first order glancing angle (the one marked "first" in Fig. 541a), the difference as regards amplitude and opposition of phase of two sets of reflections, those from sodium planes alone and those from chlorine planes alone, spaced at double- $d$  distance to the adjacent sodium and chlorine planes spaced at  $d$  distance. That is, the two sets of alternate planes, not being of equal weight and therefore not neutralising one another, are acting and giving reinforcement at twice the wave-length phase  $2\lambda$ , and the intensity observed is the differential one, taking into account the opposition of phase of vibration. The case represented at the top of the diagram (Fig. 541a), when  $b$  is equal to  $a$ , may be considered as that of sylvine KCl, when the planes at spacing  $d$  are practically all of equal mass (39 being so near 35.5). That below it, when  $b$  is equal to only half  $a$ , the second in the diagram, will then be very like the case of rock-salt, NaCl, for which the masses of alternate planes are appreciably different, namely, as 23 to 35.5.

The actual glancing angles  $\theta$  of the first order reflections from the octahedral (111) planes of sylvine, KCl, and rock-salt, NaCl, respectively, observed on a particular occasion by Profs. W. H. and W. L. Bragg<sup>1</sup> were  $18.0^\circ$  and  $9.8^\circ$ , the former being thus in the neighbourhood of twice the size of the latter, in agreement with what has just been stated, and as shown in the two top cases of Fig. 541a. The corresponding angles for the first order reflections of the cube planes (100) of the two respective salts were  $10.2^\circ$  and  $11.4^\circ$ , as observed on the same occasion, values nearly the same, and evidently of analogous nature, derived from similarly constituted atomic planes, the difference being only the slight one due to the slight increase in the spacing of the planes, as we pass from the lighter and smaller unit space-lattice cell of sodium chloride to the heavier and larger cell of potassium chloride.

Another mode of expressing this important matter, and one which treats it more generally, has been communicated to the author, just as this chapter is going to press, by Sir W. H. Bragg, and is as follows:

"The relative intensities of the various orders of reflection from a given set of planes in a crystal may be calculated in the following way, which is found to be satisfactory as a first approximation but is sure to need revision.

"At a proper angle of reflection the phase difference between the reflections from consecutive planes of similar character is a multiple of

<sup>1</sup> *Proc. Roy. Soc.*, 1913, 89, 272. The angles given as  $\theta$  in the table from which these values are quoted are probably the angles of setting of the ionisation chamber,  $2\theta$ . That this is so is confirmed by the Fig. 26 on page 89 of *X-Rays and Crystal Structure* of Profs. Bragg.

$2\pi$ . There may be several planes in the repetition pattern. Take one of these as the standard of reference and suppose that the weight of the atoms it contains is  $m_0$  per square centimetre, while the distance separating it from the next similar plane is  $d$ . Other planes may be defined as having masses  $m_1, m_2$ , etc., and as being separated from the reference plane by distances  $d_1, d_2$ , etc.

"In a reflection of the  $n$ th order, the phases of all the planes relative to the plane of reference are  $2n\pi d_1/d$ ,  $2n\pi d_2/d$  and so on. The sum of the contributions to the reflected wave by all the planes of the pattern is proportional to

$$m_0 \cos 2\pi t/T + m_1 \cos 2\pi(t/T + nd_1/d) + m_2 \cos 2\pi(t/T + nd_2/d) + \dots$$

"The intensity of the reflected wave is therefore proportional to

$$(m_0 + m_1 \cos 2n\pi d_1/d + m_2 \cos 2n\pi d_2/d + \dots)^2 \\ + (m_1 \sin 2n\pi d_1/d + m_2 \sin 2n\pi d_2/d + \dots)^2.$$

"It is found in practice that for a simple arrangement of planes, all of equal strength and equally spaced, the intensities of the different orders fall off rapidly with the number of the order for reasons not fully understood. For a first approximation it is found satisfactory to say that the intensity varies inversely as the square of the number of the order. When there are planes which vary in spacing and strength in the manner just considered, both causes of variation in the intensity of the orders have to be taken into account.

"As an example take the following simple case. Suppose the pattern to consist of planes of mass  $a$ , with planes of mass  $b$  half way between them; and consider how the relative intensities of the different orders will change as  $b$  is gradually reduced from an equality with  $a$  to zero.

"By the formula just given the intensity of the  $n$ th order is proportional to

$$(a + b \cos n\pi)^2 + (b \sin n\pi)^2,$$

that is, to  $(a+b)^2$  when  $n$  is even and  $(a-b)^2$  when  $n$  is odd.

"Hence taking into account both causes of the variation in intensities of the different orders, the following will be the system of intensities:

$$(a-b)^2, (a+b)^2/4, (a-b)^2/9, (a+b)^2/16 \dots$$

"The accompanying diagram (Fig. 541a) shows the relative intensities for different relative values of  $b$  and  $a$ .

"When  $b$  is exactly equal to  $a$ , the case considered merges into that of simple planes with half the spacing." If  $a$  be taken as unity the intensities are then 0, 1, 0,  $\frac{1}{4}$ . When  $b=0$ , however, the intensities are 1,  $\frac{1}{4}$ ,  $\frac{1}{9}$ ,  $\frac{1}{16}$ . Both cases are clearly illustrated in Fig. 541a.

**Meaning of Intensity of Spots in X-radiograms.**—It will be convenient now to revert to the Laue X-radiographic method, in which the X-rays are passed through the crystal and received after diffraction on a photographic plate placed behind the crystal, as a spot pattern. When an X-radiogram has been taken, an analysis of it is, of course, necessary, in order that its correct interpretation can be arrived



at. It is possible for a spot to appear in a position corresponding to reflection at any set of planes having integral indices ( $hkl$ ). In the pattern obtained by allowing the diffracted X-rays to fall on a photographic plate a definite number of spots appear, but they are, usually in equal sets, of very varying intensities, and by classification of the planes which reflect the principal (most intense sets of) spots of the pattern a clue can be got to the true point-system arrangement of the diffracting centres. The point-system which affords the most simple interpretation of the pattern is that which ought to be taken as representing the crystal structure. It has been shown in previous chapters that the more important planes, such as the primary facial planes, especially the axial planes and parametral planes, are those most densely packed with points (atoms), and these planes always, if operative, afford prominent and usually the strongest reflections.

There is a convenient relation between the points which are reflected in the planes belonging to any one zone of faces. The reflected beam always lies on a circular cone with apex at the crystal section, the zone axis as axis, and the direction of the primary beam as one generator. This cone cuts the photographic plate in an ellipse passing through the central point of the pattern, and all spots reflected in planes of the zone lie on it. This arrangement of the spots on ellipses (see explanation and Fig. 544 on page 664) is very obvious on an interference pattern, and the ellipses can immediately be drawn. A little calculation shows to which zone axis each ellipse must be assigned, and by marking a given spot as lying on the intersection of two ellipses the calculation of the indices of that spot is made possible. For it will be remembered (from page 88) that  $hU + kV + lW = 0$ , where  $[UVW]$  is the zone symbol.

When representing a spot pattern diagrammatically, however, it is very inconvenient to have to draw the ellipses, at the intersections of which the spots of the pattern lie. It is simpler to use an extension of the usual stereographic projection, and transform thereby the ellipses into circles. Fig. 541*b* will make it clear how this can be done. Let the section of the crystal be situated at C, the centre of the sphere represented by the circle ABP, and let the direction of the incident rays be from P to C. The rays which traverse the crystal undeviated fall on the photographic plate AD at A. Let CZ represent the direction of a zone axis. The beams reflected in planes of this zone lie on a circular cone with vertex at C, of which CZ is the axis, and CA, CB are two generators. This cone cuts the sphere in a circle of which AB is a diameter, and by the familiar property of the stereographic projection, the projection of this circle on the plane AD from the pole P is also a circle. The centre of this circle is at Z, since  $AZ = ZS'$ , Z being the point where the zone axis cuts the photographic plate.

Let the pattern of spots be supposed to be made by the diffracted beams on the sphere ABP, and this pattern projected on the plane AD from the pole P. Spots corresponding to reflection at planes of a zone now lie on a circle, having its centre at the point where the zone axis cuts the plate AD. The spot at S made by the reflected beam CB becomes a spot at S' of the transformed pattern. The distortion of the



pattern of spots by the transformation is very small, except in the regions distant from the centre, and circles are, of course, very much easier to draw than ellipses. The diagrams of spot patterns in the next two Figs. 542 and 543, and many others in this chapter, have been constructed by this method.

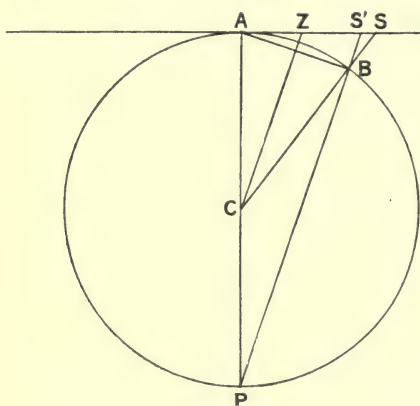


FIG 541b.

is easy when the crystal is placed symmetrically to the pencil of X-rays. A circle is then drawn with centre Z and radius ZA. This being done for each zone axis, the intersections of the circles give the stereographic projections of the reflected spots.

**Comparison of the Results of the Spectrometric and Radiographic Methods for the Chlorides of Potassium and Sodium.**—It will be interesting to see how the facts now recorded as regards the two alkali chlorides are interpreted in the Laue radiograms of these salts. They are given, drawn as above described in extended stereographic projection, from the actual radiograms, in Figs. 542 and 543, by the kindness of Sir William and Prof. W. L. Bragg. The diffraction patterns shown are those obtained when the beam of incident X-rays falls normally on the plate of rock-salt or sylvine cut parallel to a cube face (100), (010), or (001). The Fig. 543 for potassium chloride is perfectly regular, the spots for which the corresponding facial indices are given being exactly those for a simple-cube space-lattice. Fig. 542, however, for sodium chloride, is less regular, although of the same type, the spots lying on the same circles; but it is not every intersection of the circles which now shows a spot, and the intensities, represented by the sizes of the spots, vary in a manner which corresponds to the centred-face space-lattice and not to the simple-cube lattice.

It is indeed highly interesting and satisfactory to observe how the two methods of attack, those of the X-ray spectrometer and of the Laue radiogram, supplement and confirm each other. Difficulties presented by the results of one method are frequently cleared up by recourse to the other, so that it is advisable that in every research both methods should be employed and their results compared, and no conclusions arrived at which are vetoed by the result of either method alone. It must be

<sup>1</sup> *Proc. Roy. Soc.*, 1913, 89, 251.

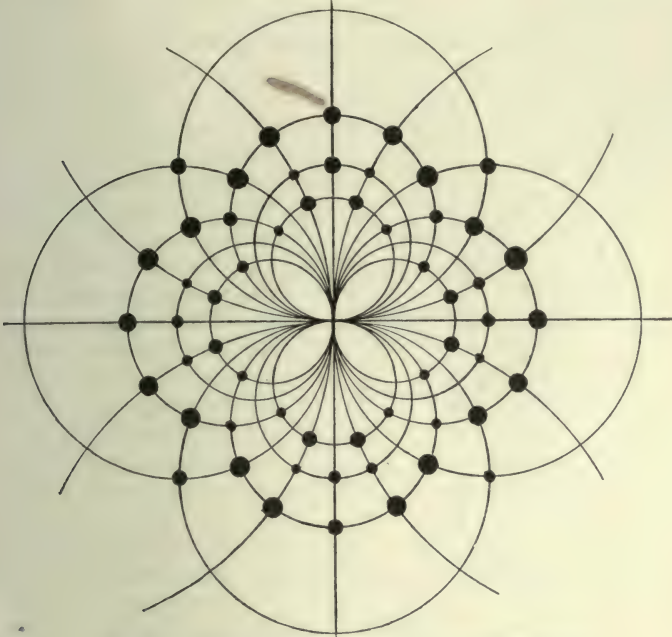


FIG. 542.—Diagrammatic X-radiogram for Sodium Chloride.

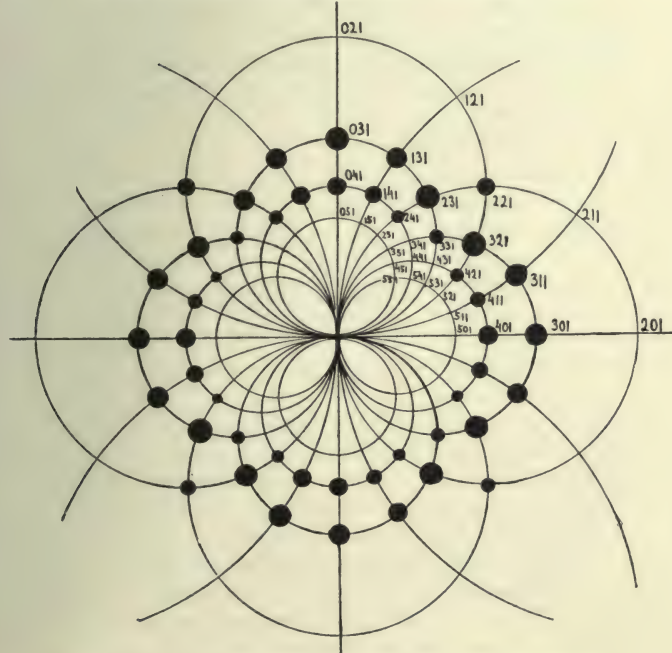


FIG 543.—Diagrammatic X-radiogram for Potassium Chloride.

remembered, however, that the Laue method is subject to more restrictions than the Bragg method, and cannot always discriminate between the holohedral class of any system of crystal symmetry and the classes of lower symmetry within that system. Direct evidence of enantio-

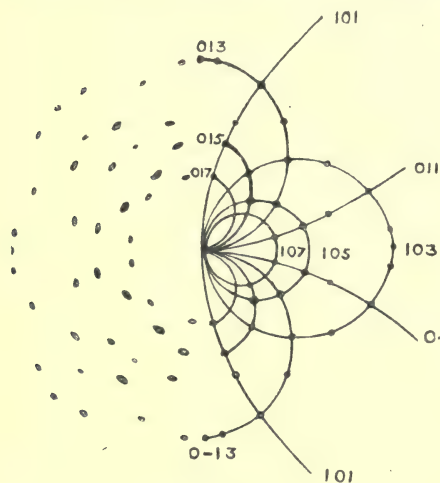


FIG. 544.

32 of the cubic system, but to class 31; yet this fact does not record itself in the radiograms given in Figs. 530, 531, and 534.

**W. L. Bragg's Explanation of the Laue Radiograms.**—The explanation of the Laue radiogram which has been given by W. L. Bragg has been already partly indicated on page 661. It is clear that the intensity of any spot depends on the number of atoms in the plane affording it; that is, the greater the reticular density of the possible crystal face corresponding to the plane, the more intense is the spot produced in the radiogram. As reticular density is also proportional to importance of face (the primary faces having the greatest reticular density), it follows

that the most important facial planes reflect the intensest spots. Each spot reflected by a plane of atoms (considered as passing through the origin and two other points) lies at the intersection of two ellipses, as shown in Fig. 544. The plane of atoms corresponding to any spot can be found from the two ellipses, for, as shown on page 661, each ellipse is the

example, the radiogram of quartz given in Fig. 535, page 646, taken from a negative sent to the author by Dr. Laue in 1912, represents either right-handed or left-handed quartz, the radiograms afforded by both enantiomorphous varieties being identical. But the X-ray spectrometric method is capable of affording many valuable indications of the detailed nature of the symmetry, and will be shown in the section on quartz to discriminate between the two varieties. Moreover, the first substance used by Laue, zinc blende, does not belong to the holohedral class

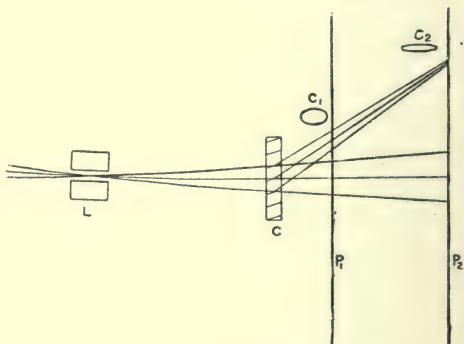


FIG. 545.



section of a cone by the plane of the photographic plate, the axis of the cone being the line joining the origin (centre of the triaxial system, and considered as one of the three points determining the plane) and the particular atom (the second or third point of the three), and the generator of the cone being the incident beam. He also explains why the spots are elliptical in shape, the amount of the ellipticity being dependent on the distance of the photographic plate from the crystal. When the two are very close the spots are round, but they become more and more elliptical as the plate is receded. This is due to the fact that the initial rays are

not strictly parallel, and the effect will be clear from Fig. 545. The vertically diverging rays from the leaden aperture  $L$  striking the reflecting planes of the upper part of the crystal  $C$  meet them at a less angle of grazing incidence than those of the lower part, and so the reflected rays converge. Horizontally diverging rays, however, diverge still more on reflection. Hence, the section of the reflected beam is an ellipse, with major axis horizontal. The effect of increase of distance of the photographic plate  $P_1$  or  $P_2$  is seen in the relative increase in the major axis of the corresponding ellipse, that of  $C_2$  corresponding to  $P_2$  being relatively much more elongated than that of  $C_1$  produced on  $P_1$ .

It cannot be made too clear that the Laue radiograms are due to diffraction by the crystal of the "white" or general radiation proceeding from an X-ray bulb, whereas a specific "monochromatic" radiation is used in the Bragg X-ray spectrometric analysis, such as that of wavelength  $0.584 \times 10^{-8}$  centimetre from the palladium anticathode. A platinum or iridium anticathode is generally used in taking the Laue radiograms, as this gives off more than a usual proportion of its X-ray energy as general radiation. Each spot in the radiogram represents the reflection of these general X-rays by a certain crystal plane ( $hkl$ ), the

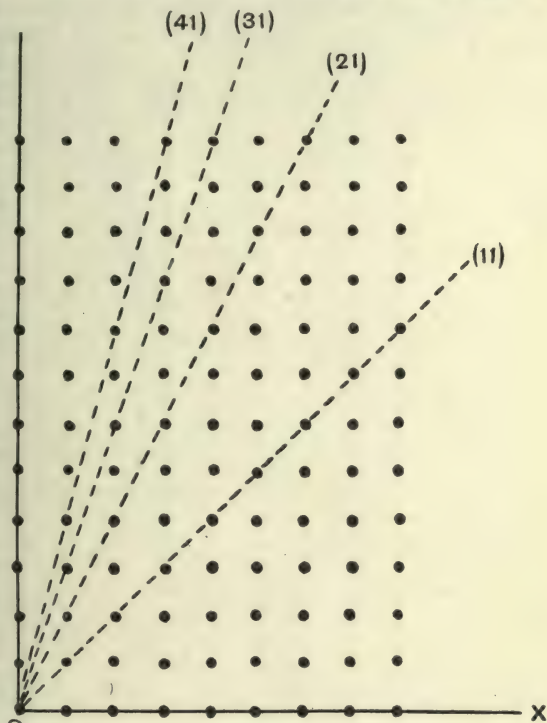


FIG. 546.

intensity of the spot corresponding to the efficiency of the reflection, determined principally by the number of atoms in the plane. It is possible to calculate from the positions of the spots the indices ( $hkl$ ) of the crystal plane, as shown on page 664. The method suffers from the fact that every spot represents the action of waves of a different wavelength (the spots would be differently coloured, if visibility and colour were attributes of X-rays), for  $d$  and  $\theta$  vary from spot to spot, and we do not know the relation between the amounts of radiation, originally present in the incident beam, for the different parts of the spectrum which are separately utilised in two different spots. Yet in many respects the Laue radiogram is of very considerable value, and it must not be forgotten that

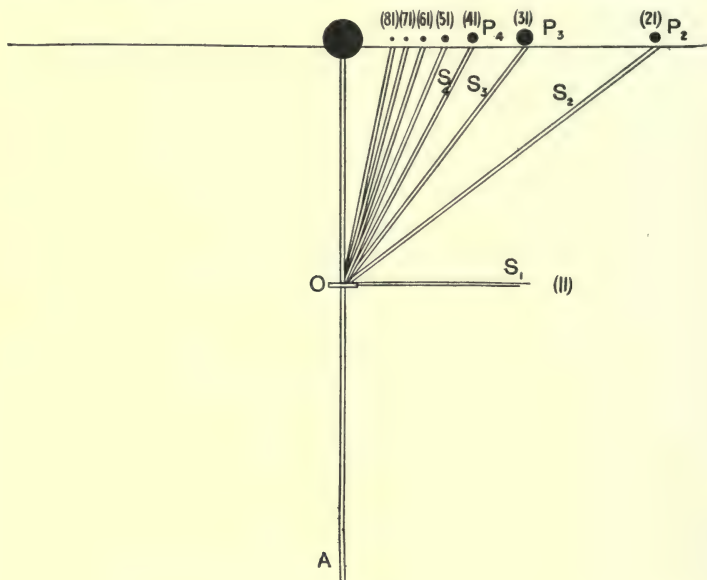


FIG. 547.

it was by the discovery of the possibility of obtaining such a remarkable thing as a radiogram of a crystal that we first became aware of the great value of X-rays as an analytical test for and diviner of crystal structure.

Figs. 546, 547, and 548 will show, as clearly as is possible to a diagram in two dimensions only, how the radiogram is produced. In Fig. 546 the atoms are all of the same kind, but in Fig. 548 they are of two kinds as in rock-salt, and it will be clear how this fact will modify the relative intensity of the spots reflected from the different planes. The large central spot at the top in Fig. 547 is, of course, that afforded by the directly transmitted incident rays from A. The crystal is supposed to be placed at O, and the rays reflected from the various planes of atoms (corresponding to the faces indicated by two of their indices) pass along the radial paths  $OS_2$ ,  $OS_3$ ,  $OS_4$ , and afford the spots  $P_2$ ,  $P_3$ ,  $P_4$ , etc., on the photographic plate, which vary in size according to the intensity of

the reflection. This latter is governed by the various causes already enumerated, namely, the wave-length and energy of the X-radiation (part of spectrum) forming this particular ray, the density of packing of the atoms in the reflecting plane, the nature of the atoms themselves, their relative masses, and their spacing.

Friedel<sup>1</sup> has made an important contribution to the theory of the Laue radiograms. He has shown that the symmetry of a radiogram should be identical with the crystal symmetry to which a centre of symmetry has been added. This is why the Laue radiograms can only distinguish eleven of the thirty-two classes of crystals. A large number of very beautiful radiograms have been published by Jaeger,<sup>2</sup> which serve particularly to illustrate and confirm Friedel's theorem; some of them are reproduced later in the chapter, for which the author's hearty thanks are due to Prof. Jaeger.

A method has been devised by R. Gross<sup>3</sup> which consists in taking a series of Laue radiograms at definite known angular positions, the crystal being mounted on a two-circle goniometer and rotated for the desired number of degrees between the exposures. The photographs are subsequently analysed on an instrument which he

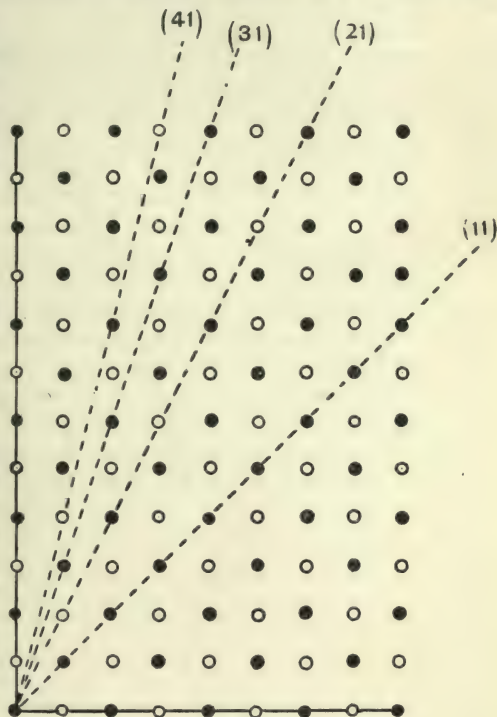


FIG. 548.

terms a "cyclometer," which enables whatever symmetry is present to be detected. The true symmetry is usually lower by a centre of symmetry, in accordance with Friedel's principle. The method is recommended for the goniometry of crystals with bad or poorly reflecting faces.

**Measurement of Absolute Dimensions of Space-lattice Cells by the Bragg Method.**—The most important advantage of the X-ray spectrometric method is, however, that we are enabled by its means to determine the actual distances (the spacings) between the planes of atoms, and thus to measure directly the distances of separation of the atoms of the space

<sup>1</sup> *Comptes rendus*, 1913, 157, 1533.

<sup>2</sup> *Proc. K. Akad. Wetensch.*, Amsterdam, 1915, 17, 1204 and 1915, 18, 542 and 559.

<sup>3</sup> *Centr. Min.*, 1920, 52.



lattice in the rectangular crystal systems, and the actual dimensions of the elementary cell of the latter, the grosser structural unit. This is, of course, an enormously important advance. It affords at once the possibility of confirming or otherwise, and of converting into absolute values, the relative values of the dimensions of the unit cells which we already possess in the topic axial ratios (molecular distance ratios), in validly comparable series of allied compounds such as isomorphous salts, not only those "eutropic" members which are formed by the interchange of family-group chemical elements of the periodic classification (such as the alkali metals), but also in most cases the other members of the series (such as those formed by ammonium and thallium). It will be shown in the sequel how remarkably exact is this confirmation, a fact which very greatly enhances the value both of topic axial ratios and of molecular volumes, which latter are confirmed as correct relative measures of the cell volumes with the same most satisfactory precision. The method of achieving this can best be explained by continuing the study of the concrete instances investigated by Sir William and Prof. W. L. Bragg, which we shall proceed to do in the next section but one.

**Spectrometric Analytical Data for the Alkali Chlorides.**—It will be useful before passing to the consideration of other crystalline substances to state briefly the data relied on by the Braggs for their conclusions regarding the structure of sodium and potassium chlorides. Starting from the fact that the principal cubic faces are of the three types (100), (110), and (111), and that the conditions are expressed by the equation  $n\lambda = 2d \sin \theta$ , we have for the first reflections from the (100) faces of potassium chloride and sodium chloride respectively,  $d_1$  and  $d_2$  being the spacings :

$$2d_1 \sin 5.22^\circ = \lambda, \quad \text{and} \quad 2d_2 \sin 5.9^\circ = \lambda, \text{ from which :}$$

$$d_1 = 5.48\lambda, \quad \text{and} \quad d_2 = 4.85\lambda.$$

Now the ratio of the true volumes of the elementary cells, that is, of  $d^3$  in each case, is that of the molecular volumes  $\frac{M}{\delta}$  in each case (the molecular weight to the density, the latter being written as  $\delta$  instead of the usual  $d$  to avoid confusion with the spacing  $d$ ), so that we now have :

$$\frac{d_1^3}{d_2^3} = \frac{\text{Mol. vol. of KCl}}{\text{Mol. vol. of NaCl}} = \frac{M_1/\delta_1}{M_2/\delta_2}.$$

Rearranging and extracting cube roots we obtain :

$$d_1 \cdot \sqrt[3]{\frac{\delta_1}{M_1}} = d_2 \cdot \sqrt[3]{\frac{\delta_2}{M_2}}.$$

Therefore  $d \sqrt[3]{\frac{\delta}{M}}$  should be the same for the two salts. On testing this it is found that for KCl the value is  $1.63\lambda$ , and for NaCl it is  $1.62\lambda$ . Moreover, on extending the observations to potassium bromide, another member of this group of haloid salts, the same value  $1.63\lambda$  is again found. Hence, it is clear that the structures of the three salts are analogous.

Passing next to the consideration of the type of cubic space-lattice which is present, the following relations express the conditions for the three lattices :

$$\text{For the simple-cube lattice } \frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} = 1 : \sqrt{2} : \sqrt{3},$$

$$\text{For the cube-centred lattice } ,, ,, ,, 1 : \frac{1}{\sqrt{2}} : \sqrt{3},$$

$$\text{For the face-centred-cube lattice } ,, ,, ,, 1 : \sqrt{2} : \frac{\sqrt{3}}{2}.$$

Now for potassium chloride :

$$\begin{aligned} \frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} &= \sin 5^{\circ} \cdot 22 : \sin 7^{\circ} \cdot 30 : \sin 9^{\circ} \cdot 05, \\ &= 0 \cdot 0910 : 0 \cdot 1272 : 0 \cdot 1570, \\ &= 1 : \sqrt{2} : \sqrt{3}, \end{aligned}$$

so that the space-lattice of potassium chloride is that of the simple cube. The diffraction spectra have been shown to agree with this conclusion.

In the case of sodium chloride the diffraction spectra do not tally with this conception. Hence, we are bound to conclude that the diffracting centres arranged on a cube lattice in potassium chloride are not molecules of KCl, but atoms of the two elements. For if they were molecules so arranged on that lattice the sodium chloride molecules would be expected to be similarly arranged on a simple-cube lattice. Indeed we are driven to the conclusion already recorded that it is the atoms with which we are dealing, and that the atoms of K and Cl act so similarly, as if only one kind of atom were present, because their atomic weights (and therefore masses acting as diffracting centres) are almost identical. For, as already mentioned, the intensity of reflection of X-rays from an atom has been found to be proportional to its mass. This very important principle may also be stated thus: The amplitude of the waves reflected by each net-plane of the space-lattice is nearly proportional to the total mass of the atoms lying in that net-plane. In NaCl, KBr, and KI the atoms of the two elements are not alike in mass, and the face-centred space-lattice which obtains for these three haloid salts corresponds to the atoms of one kind only, a conclusion which has already been recorded. The ratios of the reciprocals of the spacings for the three primary-face planes (100), (110), and (111) are  $1 : \sqrt{2} : \frac{\sqrt{3}}{2}$  for

each of these salts, confirming the presence of a face-centred cube lattice.

W. Voigt<sup>1</sup> has shown that this structure now revealed by X-rays for NaCl and KCl, in which each atom species (chemical element) forms the face-centred cubic space-lattice No. 3 (Fig. 454, page 583), is that of Sohncke's regular point-system No. 55 or No. 60 (pages 616 and 618), the octahedral 12- or 24-pointer, concentrated (specialised) into a single atom.

<sup>1</sup> *Phys. Zeitschr.*, 1918, 19, 446.

**Zinc Blende.**—A crystal of this mineral is illustrated in Fig. 113 (page 162). It consists of a combination of the two tetrahedra  $\{111\}$  and  $\{1\bar{1}1\}$ , developed clearly to different extents and therefore not holohedral faces of an octahedron, with small faces of the cube  $\{100\}$ . For zinc blende,  $\text{ZnS}$ , has been shown (page 162) to belong to the hexakis tetrahedral class 3l of the cubic system. The substance is highly interesting as having been the first studied by Laue, and reproductions of his radiograms have been given in Figs. 530, 531, and 534, the two former having been taken with a cube face adjusted and Fig. 534 with an apparent octahedron (really a tetrahedron) face perpendicular to the incident X-rays. When examined by the spectrometric method, the first order spectra afford the same relative values for the three primary faces (100), (110), and (111) as in the case of rock-salt, and the ratio of the sines of their angles of reflection is  $1 : \sqrt{2} : \frac{\sqrt{3}}{2}$ , corresponding to the face-centred cube lattice. Also, taking the molecular weight  $M$  as 97 and the density  $\delta$  as 4.06, we find that

$$d \sqrt[3]{\frac{\delta}{M}} = 1.64\lambda.$$

Hence, there are as many atoms of zinc and sulphur as of sodium and chlorine to the crystal-unit cubes of zinc blende and rock-salt. The structures are not identical, however, for the spectra agree with the supposition that while the zinc atoms lie on one face-centred cube lattice and the sulphur atoms likewise lie on a lattice of this same type, the relative positions of the two lattices are not the same as in rock-salt. The arrangement for zinc blende proves to be that shown in Fig. 549.

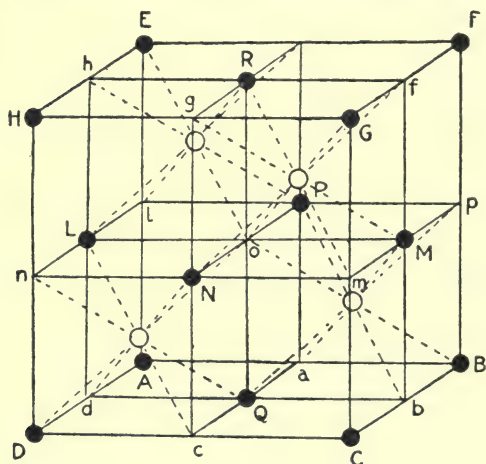


FIG. 549.—The Structure of Zinc Blende.

It will be seen that the zinc atoms (solid points) are placed at the corners and centres of the large cube faces, marked by capital letters, like the sodium atoms in sodium chloride. But the sulphur atoms (rings) occupy the centres of four alternate small cubes, of the eight such small cubes which make up the large unit-structural cube. The nodes of the lattice marked by small letters are unoccupied by atoms. Although the figure does not render the fact plain,

as only one large unit cube is represented, it is nevertheless true that when the structure is considered on a model showing several



such neighbouring large cubes in position adjacent to each other, the sulphur atoms are then seen to lie really on a face-centred cube lattice like the zinc atoms. The (111) planes are now of a new type, for the distance from zinc atom to zinc atom is four times that separating zinc and sulphur atoms. The atomic weight of zinc, 65, is almost exactly double that of sulphur, 32, and instead of interfering, the reflections from the sulphur planes of atoms which alternate between the zinc planes reinforce slightly the reflections from the zinc planes, in the case of the first order reflections. With the second order reflections the case is different, the waves from the sulphur planes being exactly out of phase with those from the zinc planes. For the successive wave-trains from the zinc planes have a phase difference of  $4\pi$ , while the phase difference corresponding to successive zinc and sulphur planes is one-fourth of this, namely  $\pi$ , which means that the two trains are in opposite phases, and this second order reflection is thus very weak, being actually weaker than the third order reflection. It would disappear altogether if the atomic weights (masses) of zinc and sulphur were alike. This all bears out the structure which has been represented for zinc blende in Fig. 549.

W. Voigt<sup>1</sup> has pointed out that this structure now revealed by X-rays for zinc blende falls under Sohncke's regular point-system No. 55, the octahedral 12-pointer (Fig. 517 on page 616), in which the zinc atoms have their initial atom at the construction zero-point, the left bottom front corner of the cube, and the sulphur atoms have their initial one in the centre of an 8-pointer cubelet (one of the small cubes into which the large zinc cube is subdivided).

**The Diamond.**—The next substance studied was the diamond, which has afforded results of striking interest. This beautiful form of the element carbon has been shown (on pages 155 and 502) to belong in all probability to the holohedral class 32 of the cubic system, although it has in the past been frequently classified as of the hexakis tetrahedral class 31. Now it is remarkable that if both the zinc atoms and the sulphur atoms in zinc blende, as represented in Fig. 549, be replaced by carbon atoms, we obtain the structure of the diamond. That is, we put  $2C = ZnS$ . All the atoms are now those of carbon, but they are arranged in two face-centred cube lattices, the atomic points of one of which occupy the corners and face-centres of the main large cube, while the atomic centres of the other are situated at the centres of the alternate small cubes of the eight which go to make up the large structural-unit and space-lattice-cell cube. One of the large cubes is shown in Fig. 550, the complementary (small letter) one to that in Fig. 549 being chosen; and one of the eight constituent small cubes in Fig. 551, the numbers enabling the one chosen to be identified. Another figure of diamond structure is given at A in Fig. 556 on page 676.

Another mode of describing the structure is that it consists of a superposition of two face-centred cubic lattices, one of which is obtained from the other by translating it rigidly along a cube diagonal for one-quarter

<sup>1</sup> *Phys. Zeitschr.*, 1918, 19, 446.

of the length of the diagonal. Each point of both lattices is occupied by a carbon atom. The result is that each carbon atom occupies the centre of a regular tetrahedron, the four corners of which are occupied by the four nearest neighbours of that atom.

The atoms being now all alike, the differential effect of atomic weight no longer intervenes, and the effect on the second order spectrum from the (111) planes is the purely natural one of extinction, corresponding to the exact one-quarter phase difference. Moreover, the first order spectrum from the (100) planes also disappears, as all the planes of atoms parallel to the cube faces are now composed of identical chemical matter. The (110) planes are  $\sqrt{2}$  times and the (111) planes  $4/\sqrt{3}$  times as far apart as the (100) planes, and the positions and intensities of the spectra from

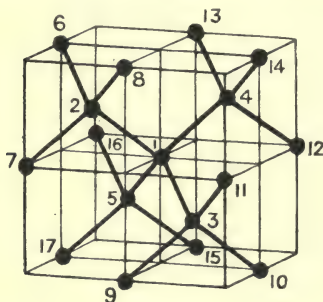


FIG. 550.

The Structure of Diamond.

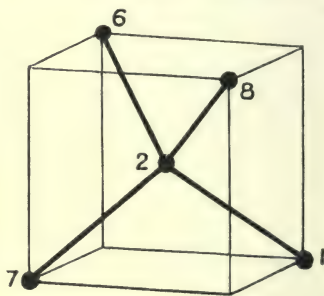


FIG. 551.

each set of planes agree completely with the structure shown in Figs. 550 and 551. To test it further, however, it should yield a value for  $d\sqrt[3]{\frac{\delta}{M}}$  about  $1.63\lambda$ . As  $\text{ZnS} = 2\text{C}$ ,  $M$  will be  $2 \times 12 = 24$ ;  $\delta$  the density is  $3.51$ .<sup>1</sup> The  $d$  in zinc blende was calculated from the first order spectrum of (100), but this now is absent for the diamond, and the  $d$  for diamond is thus doubled. Working this out for the palladium ray it is found that :

$$2\lambda = 2d \sin 19.0^\circ, \text{ from which}$$

$$d = 3.06\lambda, \text{ and } d\sqrt[3]{\frac{\delta}{M}} = 1.62\lambda,$$

which agrees adequately with the average value  $1.63\lambda$  for the structure proposed, and proves that the diamond and zinc blende do possess the same number of atoms in each structural-unit cube.

The structure of diamond as given in the Figures 550 and 551 may be derived by taking a face-centred cubic space-lattice A, and imagining it to be translated parallel to itself along a cube diagonal for one-quarter the length of that diagonal. The new position is that of the second lattice B which is to be taken, and the points of both the lattices A and B taken together make up the positions of the carbon atoms. In Figs.

<sup>1</sup> According to L. Silberstein the mean of all the best determinations of the specific gravity of the diamond is  $3.515$  (*Phil. Mag.*, 1919, 37, 405).

550 and 551 links are drawn between the atoms and it will be seen that each carbon atom is linked up with four other carbon atoms which surround it. This will be even clearer if a model be constructed, and set up on an octahedral (111) plane as shown in Fig. 552. Moreover the balls build up a tetrahedron resting on one of the faces (111). In addition to its four immediate neighbours at the distance  $\sqrt{3} \cdot a/2$ , where  $a$  represents the edge of the small cube, each carbon atom is symmetrically surrounded by twelve other atoms at the greater distance  $\sqrt{2} \cdot a$ . It has been pointed out by Föppl<sup>1</sup> that the sphere of influence of each atom is accordingly a regular tetrahedron, each of the four corners of which has been modified by the rhombic dodecahedron to the extent that the triangular faces of the original tetrahedron have become regular hexagons. This modified tetrahedron deviates considerably from the form of a sphere, so that the diamond structure corresponds to that of a very loosely packed system of spheres, a fact which is entirely opposed to the validity of the Barlow-Pope theory of valency volumes, which requires closely packed spheres.

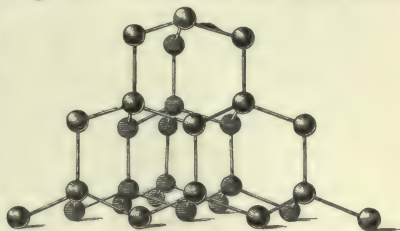
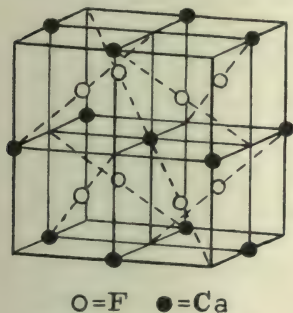


FIG. 552.—Model of the Diamond Structure.

According to W. Voigt,<sup>2</sup> Sir W. H. Bragg's arrangement of the carbon atoms in diamond may be described as composed of two identical face-centred space-lattices No. 3 (Fig. 454, page 583), one of which has received a quarter translation. The type is that of Sohncke's No 64, the right regular four-point screw system (Fig. 524 on page 620), specialised so that the construction zero-point is the position of the initial carbon atom; this type No. 64 also agrees perfectly with the tetrahedral arrangement of the four valencies of the carbon atom as present in diamond.

**Fluor-spar.**—This mineral,  $\text{CaF}_2$ , which is holohedral cubic, of class 32 symmetry, has also been studied by Bragg, and its X-ray spectra found to be very like those of the diamond. The calcium atoms are arranged in a face-centred cube lattice, while the fluorine atoms occupy the centres of the small cubes. For in this case there are two atoms of the negative element, fluorine, to every atom of the positive element, calcium; so that not only alternate cubelets, as in cases of zinc blende and diamond, but all the cubelets are occupied. The arrangement is shown in Fig 553. The planes containing calcium atoms are alternated with planes containing twice as many fluorine atoms, when one considers planes parallel to the cube faces  $\{100\}$ . These



○ = F    ● = Ca

FIG. 553.—The Structure of Fluor-spar.

planes are found to be the same in reflecting power for X-rays; for

<sup>1</sup> *Phys. Zeitschr.*, 1914, 15, 191.

<sup>2</sup> *Phys. Zeitschr.*, 1918, 19, 446.



the first order spectrum, which might be expected to be reflected by planes parallel to (100), is practically extinguished, the two opposing planes being of almost exactly equal intensity. Now, the atomic weight of calcium is 40, and that of fluorine 19; so that two fluorine atoms, together making a mass of 38, balance the mass 40 of the single atom of calcium. This is one more very perfect example of the Bragg principle, that the reflecting power of a plane of atoms for X-rays is proportional to its mass per unit area. The quantity  $d \sqrt[3]{\frac{\delta}{M}}$  has also the usual value in the case of fluor-spar, namely  $1.62\lambda$ , further agreeing with the structure above stated.

According to Voigt (*loc. cit.*) this structure of calcium fluoride falls under Sohncke's type No. 60 (Fig. 520 on page 618), the octahedral 24-pointer.

**Iron Pyrites.**—The spectra of this cubic mineral,  $\text{FeS}_2$ , of the dyakis dodecahedral class 30 (see page 164), are more complicated than those of the cases yet considered. The sines of the glancing angles ( $13^\circ$ ,  $18^\circ.1$ ,  $11^\circ.7$ ) of the first order spectrum from the three primary planes (100), (110), and (111) bear the ratio  $1 : \sqrt{2} : \frac{\sqrt{3}}{2}$ , which is characteristic of the face-centred cubic lattice, and calculation shows that one molecule of

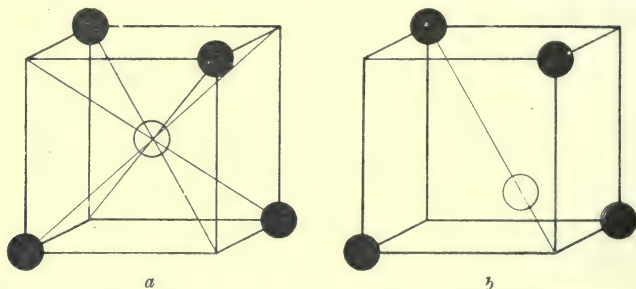


FIG. 554.—Derivation of the Structure of Iron Pyrites from that of Fluor-spar.

$\text{FeS}_2$  is associated with each point of the lattice. But the same arrangement as in fluor-spar will not fit the spectra. A cubelet of fluor-spar is represented at *a* in Fig. 554. In pyrites the internal sulphur atom is not central, as was the fluorine in fluor-spar, but is moved along one of the diagonals, as represented in Fig. 554 at *b*. The iron atoms are at the corners, like the calcium atoms of fluor-spar. Each sulphur atom has only one trigonal axis passing through it, whereas the fluorine had four such axes. A series of non-intersecting threefold axes of symmetry are chosen, one passing through each iron atom, so that each small cube of the large structural-unit cube shown in Fig. 555 has a single diagonal which is a threefold axis, on which the sulphur atom is situated, at a point near the empty cube corner. The exact position of the point was given by Bragg as dividing the diagonal in the ratio 1 : 4. The symmetry is, of course, cubic, but that of the class 30 (dyakis dodecahedral or pyritohedral),

as is well known from other considerations. It is extremely interesting that the Bragg method should thus indicate not only the system but the class, even when the latter is a difficult one of lower degree. The Braggs have also shown that hauerite,  $\text{MnS}_2$ , and cobaltite,  $\text{CoAsS}$ , are built up in a manner similar to pyrites, but with the possibility that cobaltite (cobalt glance) belongs to the lower class 28, the tetrahedral-pentagonal-dodecahedral. An excellent model of pyrites is illustrated at *b* in Fig. 584*b* on page 715.

Ewald,<sup>1</sup> in an exhaustive analysis of Laue's radiograms for iron pyrites, has shown that the ratio of the diagonal position is nearer 2:7 than 1:4, and also that the isomorphous mineral **Hauerite**,  $\text{MnS}_2$ , affords similar radiograms and possesses a similar structure, and that the ratio in this case is exactly 1:4.

W. Voigt (*loc. cit.*) has shown that here for the first time we meet with a structure in pyrites and hauerite which involves coincidence movements (Deckoperationen) of the second kind.  $\text{FeS}_2$  corresponds to Sohncke's type No. 57*a*(*a*), one of the special cases of No. 57 (Fig. 519 on page 618), the regular alternating 2-point screw system, the Schönflies system  $T_h$ <sup>6</sup>. Cobalt glance,  $\text{CoAsS}$ , is likewise conformable to this same type, both the sulphur and arsenic atoms being arranged in accordance with Sohncke's No. 57.

It is also of interest to note that not only do the combined Laue and Bragg methods give us the nature and absolute dimensions of the elementary cell of the space-lattice of the structure, but also the details of the atomic internal structure within the cell. In the case of pyrites and hauerite, for instance, this intimate atomic structure proves to be one of the Fedorov-Schönflies point-systems involving second kind coincidence movements, namely, the asymmorphous system  $(25)x'$  of Fedorov's classification, according to Voigt a specialised form of Sohncke's No. 57 (Fig. 519). Of the cubic substances now dealt with, rock-salt, fluor-spar, and diamond are of holohedral class 32 symmetry; zinc blende is of class 31 symmetry, hexakis tetrahedral; and pyrites and hauerite are of class 30 symmetry, dyakis dodecahedral. The structures revealed by the X-ray spectrometric method are precisely in accordance with these facts of symmetry, and in all the cases but those of pyrites and its two analogues hauerite and cobaltite involve only coincidence movements of the first kind, and thus correspond to Sohncke regular point-systems. In this respect the method carries us a distinct step beyond the Laue radiographic method, which goes no further than the system of symmetry. Ewald, however, has indicated increased possibilities for the radiographic method, and in any case the indications of the radiograms fully confirm, as far as they go, the results afforded by the spectrometric method.

**Spinel Group.**—This important group of cubic (holohedral class 32)

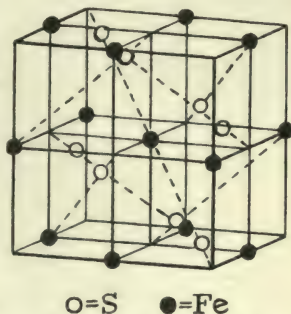


Fig. 555.—The Structure of Iron Pyrites.

<sup>1</sup> *Phys. Zeitschr.*, 1914, 15, 399.

minerals of the general formula  $R''R_2'''O_4$ , including magnetite  $Fe_3O_4$  and ruby-spinel  $MgAl_2O_4$ , has also been studied by the Braggs and simultaneously by Nishikawa.<sup>1</sup> The unit cube of the structure contains one molecule  $R''R_2'''O_4$ , and the structure has the peculiarity that the rhombic dodecahedron planes (110) are the most widely spaced. While the oxygen atoms play an insignificant part in the X-ray behaviour of magnetite, the iron atoms being relatively heavy (56 as against 16), they are of more importance in spinel as both magnesium (24) and aluminium (27) are exceptionally light metals. The structure of magnetite which at once suggested itself to Sir William Bragg was similar to that of diamond,

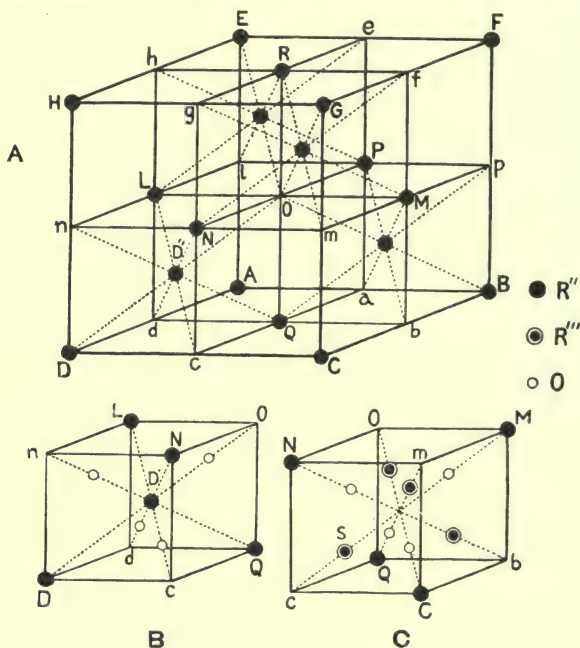


FIG. 556.—The Structure of Magnetite.

the carbon atoms being replaced by  $Fe_3O_4$  molecules, and he arrived at the structure shown at A in Fig. 556. Nishikawa, quite independently, using the Laue method but with unsymmetrical as well as symmetrical photographic exposures, arrived at the same structure, by direct comparisons with radiograms similarly obtained with diamond.

The carbon atoms are replaced by  $R''$  atoms. The structure of the diamond is reproduced at A in the figure, but the dots, marked by capital letters, must now be assumed to represent  $R''$  atoms. The two lower cubelets at B and C are separate drawings of the two front-lower small cubes of A, the two alternating types of cubelet, and they both show the oxygen atoms; but only the cubelet at B has a  $R''$  atom (just as diamond has a carbon atom only at the centres of alternate cubelets). The  $R'''$  atoms

<sup>1</sup> *Tokyo Sugaku-Buturigakkwai Kizi*, 1915, 8, 199.



are situated in the cubelets which are vacant in diamond, and are, therefore, shown at C. The whole assemblage possesses tetragonal screw axes and glide planes of symmetry, and belongs to the class  $O_h^7$  of Schönflies.

It is particularly interesting that Nishikawa shows that these truly isomorphous (in the absolutely literal sense of the word) crystals, exhibiting the identical external angles of the forms of the cubic system, possess individual internal characteristics. For the distance in ruby-spinel of the oxygen atom from the  $R''$  atom Mg is 0.36 of the distance of the  $R'''$  atom Al lying on the same diagonal (CO for instance) from the same Mg atom at C, whereas in magnetite the corresponding ratio is 0.34. The similar slight internal difference between iron pyrites,  $FeS_2$ , and hauerite,  $MnS_2$ , discovered by Ewald, may be taken as another instance confirmative of this conclusion of Nishikawa.

**Cuprite.**—Another cubic mineral interesting in this respect, the discrimination between holohedrism and the so-called "hemihedrism," namely cuprite,  $Cu_2O$ , has also been investigated by Bragg. It is supposed to belong to class 29, the pentagonal icositetrahedral class, which is holoaxial but possesses no planes of symmetry. The X-ray spectra indicate the structure shown in Fig. 557, the copper atoms being on a centred-face cubic lattice and the oxygen atoms on a centred-cube lattice. The indications are holohedral. In any case the "hemihedrism" must be very slight, as in the case of potassium chloride, which is also supposed, on evidence very difficult to reproduce, to belong to this same class 29. The evidence in question is the very rare crystallisation in the pentagonal icositetrahedron {931}, and formation of etch-figures of this form. Similar evidence in the case of rock-salt has proved to have been misleading; for more prolonged action of a solvent resulted in holohedral etch-figures being obtained. This new evidence of the X-ray analysis, as to the more probable holohedrism of potassium chloride and cuprite, is thus very welcome and valuable. The case of ammonium

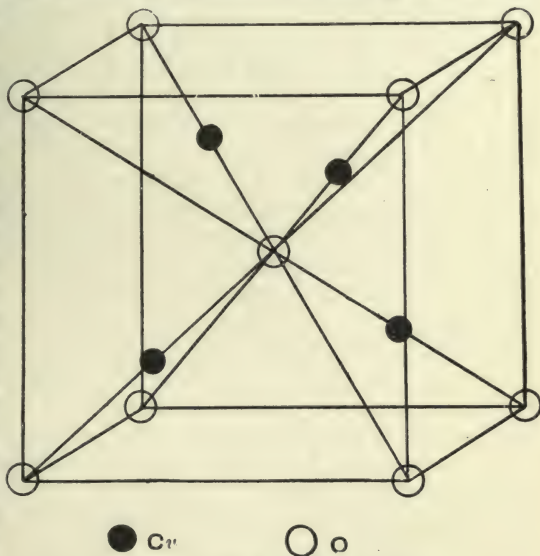


FIG. 557.—The Structure of Cuprite.

chloride is not comparable, for while the unit cube of its structure proves to have one molecule  $NH_4Cl$  in it, that of potassium chloride has only half a molecule of  $KCl$  in it, so that there is not truly comparable

isomorphism. In ammonium chloride the chlorine atoms are arranged on a simple-cube lattice, at the corners, and the nitrogen atoms are at the centres of these cubes; but the hydrogen atoms are so light that they do not affect the X-rays sufficiently for their positions to be determined.

**Copper.**—The simplest example of cubic structure is afforded by a number of the metals. Thus, first in point of time, the positions of the copper atoms in native copper crystals have been ascertained. The structure proves to be that of the centred-face cube lattice, purely and simply, the copper atoms lying at the corners of the unit cube and at the centre of each face, the structure already illustrated in Fig. 541 on page 656. The side of the elementary cube of copper is  $3.61 \times 10^{-8}$  centimetre.

Vegard<sup>1</sup> has also shown that silver, gold, and lead crystals possess a similar structure, their lattices all being those of the centred-face cube. The side of the elementary cube of gold is  $4.07 \times 10^{-8}$  centimetre, that of silver  $4.06 \times 10^{-8}$  centimetre, and that of lead  $4.91 \times 10^{-8}$  centimetre.

W. Voigt<sup>2</sup> has shown that this simple structure for copper, silver, gold, and lead is that of the Sohncke regular point-system No. 55 or No. 60 (see Figs. 517 and 520 on pages 616 and 618), the octahedral 12- or 24-pointer, concentrated (specialised) into a single atom and therefore reduced to the face-centred cubic space-lattice No. 3 (Fig. 454, page 583).

P. Scherrer<sup>3</sup> has investigated the structure of metallic aluminium by the method of Debye and Scherrer described on page 689, and has found it to be also cubic, the atoms being arranged in a simple face-centred lattice, the length of the side of the elementary cube being  $4.07 \times 10^{-8}$  centimetre. The structure of nickel and thorium has been investigated by H. Bohlin,<sup>4</sup> by the method of Debye and Scherrer, page 689, but using the powdered crystalline metals compressed into the form of a cylindrical arc, whereby the interference lines were considerably sharpened. He found the structure to be that of the face-centred cube in both cases. (For the structure of nine other cubic metals see page 693.)

**The Alums.**—At the other extreme, probably the most complicated substances yet tackled are the alums. These important salts have been shown on page 165 to crystallise in the dyakis dodecahedral class 30 of the cubic system. Potassium alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , ammonium alum,  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , iron alum,  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , and chrome alum,  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , have been studied by the Bragg method by L. Vegard and H. Schjelderup.<sup>5</sup> The main interest of this work lies in the complication introduced by the presence of water of crystallisation, and especially of so much of it. The idea was to discover how the crystal water is arranged in the structure. Although the molecule is so large and complicated, the crystal system is cubic, which materially reduced the difficulty. Employing the rhodium line  $\lambda = 0.607 \times 10^{-8}$  centimetre, the glancing angles of reflection and the intensities were measured for the planes of the cube (100), rhombic dodecahedron (110), and octahedron (111),

<sup>1</sup> *Phil. Mag.*, 1916, 31, 83, and 1916, 32, 66.

<sup>2</sup> *Phys. Zeitschr.*, 1918, 19, 446.

<sup>3</sup> *Ibid.*, 1918, 19, 23.

<sup>4</sup> *Ann. der Physik*, 1920, 61, 421.

<sup>5</sup> *Ibid.*, 1917, 54, 146.

and as the result the arrangement of the metallic, sulphur, and oxygen atoms in the structure have been arrived at, not, it is true, directly, but by a process of elimination of all the impossible arrangements having regard to the angles and intensities observed. The net result is that the 24 molecules of water of crystallisation in the double molecule  $K_2Al_2(SO_4)_4 \cdot 24H_2O$  (which appears to be the correct constitutional formula) are divided into six groups of  $4H_2O$ , which are cubically disposed with reference to the four tetrahedrally arranged sulphur atoms. The observed relations between the glancing angles and the intensities of the X-radiations from rhodium do not indicate any distinction between the water of crystallisation and the other constituents of the alum. In

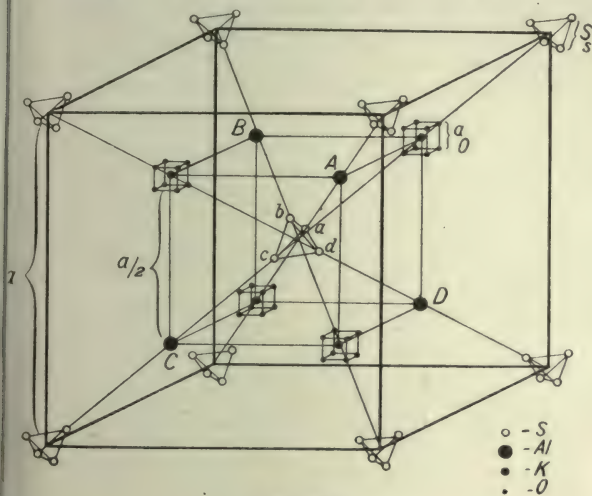


FIG. 558.

The Structure of Alum.

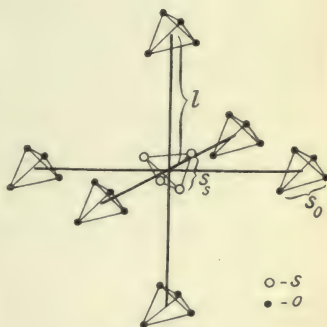


FIG. 559.

confirmation of this we have the fact that the removal of any crystal water is destructive of the crystal structure and of the alum as such.

The two Figs. 558 and 559, reproduced from the memoir, will assist in rendering the structure as clear as possible for so complicated a case. Photographs of models are also given in the memoir, but these are only confusing from their excess of complication.

The ratio for the three primary planes was :

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \sqrt{2} : \frac{2}{\sqrt{3}}.$$

The number of molecules of  $RM(SO_4)_2 \cdot 12H_2O$  to the elementary cube of side  $d_{(100)}$  is one-half, or four to the large cube including the whole structure shown in Fig. 558. This corresponds to the arrangement of the metallic atoms potassium and aluminium (taking potash alum as a type) in a face-centred cube lattice, and the arrangement shown in the Fig. 558 best represents the observations. The side of the large cube is twice that of the small one of  $d_{(100)}$ . The construction points of the four elementary



lattices of aluminium form the corners of a tetrahedron ABCD. Similarly, the construction points of the potassium atoms lie at four of the corners of a cube of side  $a/2$ , the aluminium atoms being at the alternate corners. The sulphur atoms lie in two groups of four, forming the corners of a tetrahedron  $abcd$ , and, considering each group as a single element, form a centred cube, composed of two elementary lattices, the tetrahedra of which are rotated  $90^\circ$  with respect to each other. The centres of these sulphur tetrahedra lie in the centre of the K - Al tetrahedra.

To each potassium or aluminium atom there correspond eight oxygen atoms of the  $\text{SO}_4$  groups, which are situated at the corners of a little cubelet centred about the potassium atom.

As regards the water, to each group of four sulphur atoms there belong 24 water molecules, arranged in six groups of four each. The oxygen atoms of each group form the corners of a tetrahedron, and the six groups are octahedrally arranged around the sulphur tetrahedra at the ends of the cubic axes, as shown in Fig. 559. The position of the hydrogen atoms could not be fixed definitely, as these atoms are so light, so feebly reflective, and so widely disseminated in the structure; but they lie in all probability in pairs on a line through each oxygen atom and the centre of the opposite face of the oxygen tetrahedron.

Any distinction between crystal water and water of constitution is thus negatived as regards the solid crystal structure.

These experimental results have been accepted, but the deductions as to structure criticised, by P. Niggli.<sup>1</sup> He first points out what is very true, that X-ray workers with crystals must take more note of the 230 types of possible homogeneous crystal structure, for their results must, if they are trustworthy, coincide with one or other of these possible arrangements of atoms or points. He next shows that the ratio  $1 : \sqrt{2} : \sqrt[3]{2}$  found

by Vegard and Schjelderup indicates the type  $\mathfrak{T}_n^2$  of Schönflies (the second type of the group  $T^h$  given in the table on page 624, as the Schönflies class symbol of crystal class 30), which does not altogether agree with the structure suggested by them. The suggestions of Niggli are, however, somewhat vague and uncertain, and do not afford a definite basis for a different structure. Doubtless, however, Vegard and Schjelderup will take note of the criticisms of Niggli, which may help them either to confirm or modify, especially as regards the position of the water molecules, the structure as given in Figs. 558 and 559.

The whole of the crystalline substances dealt with as regards their crystal structure in the preceding pages of this chapter have belonged to the cubic system. In succeeding pages substances crystallising in other systems of symmetry will be considered.

**Trigonal Crystals—The Calcite Group.**—Sir W. H. Bragg has made a comprehensive study of Iceland spar,  $\text{CaCO}_3$ , and of some of its analogues, magnesite  $\text{MgCO}_3$ , chalybite  $\text{FeCO}_3$ , rhodochrosite  $\text{MnCO}_3$ , and calamine  $\text{ZnCO}_3$ , all of which prove to have the rhombohedral structure correspond-

<sup>1</sup> *Phys. Zeitschr.*, 1918, 19, 225.

ing to class 21 (see page 344) expected of them. The unit rhomb is the elementary space-lattice cell. The spacing of the planes of atoms parallel to the faces of the rhomb  $\{100\}$  have been determined from the angles at which X-rays of known wave-length (the palladium ray) are reflected by any face of the rhomb. The angle of reflection for calcite was  $5^{\circ}35'$ . Substituting this in the usual formula one obtains :

$$d_{(100)} = 3.07 \times 10^{-8} \text{ cm.}$$

As the angular dimensions of the rhomb are known, this possible spacing affords for the volume of the elementary cell :  $1.08 \times d_{(100)}^3$ . The density of calcite being 2.71 the mass contained in this elementary cell would be :

$$2.71 \times 1.08 \times 3.07^3 \times 10^{-24} = 8.50 \times 10^{-23} \text{ grammes.}$$

Now the mass of a molecule of  $\text{CaCO}_3$  is as follows, knowing that the mass of a hydrogen atom =  $1.64 \times 10^{-24}$  :

$$(40 + 12 + 48) \times 1.64 \times 10^{-24} = 16.4 \times 10^{-23} \text{ grammes.}$$

Hence, as the result of this latter calculation is double that of the former one, there would be only half a molecule of  $\text{CaCO}_3$  in the elementary cell if the supposition above made were substantiated. The true space-lattice, however, on which the calcium atoms (as representing whole molecules) are built must, therefore, be one composed of cells of the same shape as this rhomb but of twice the linear dimensions and eight times the volume. There must be a point at each corner and one at the centre of every face, like a distorted cube of rock-salt. One molecule of  $\text{CaCO}_3$  will be arranged round each point, and there are then four molecules of  $\text{CaCO}_3$  to each face-centred cell. The distance from each other of the parallel-side planes of the rhombohedral cell will be twice that given by  $d_{(100)}$ .

These considerations thus enable it to be surmised that four molecules of  $\text{CaCO}_3$  go to the unit space-lattice cell, and the calculations are then to be recommenced on this basis as under, using the new probable double value of  $d_{(100)}$  :

$$\text{Volume of unit cell : } 1.08 \times (2d_{(100)})^3.$$

$$\text{Known density of calcite : } 2.71.$$

$$\text{Mass in unit cell : } 1.08 \times (2d_{(100)})^3 \times 2.71 \text{ grammes.}$$

$$\text{Content of cell : Four } \text{CaCO}_3 \text{ molecules each weighing } 164 \times 10^{-24} \text{ grammes.}$$

$$\text{Therefore, } 1.08 \times 2d_{(100)}^3 \times 2.71 = 4 \times 164 \times 10^{-24},$$

$$\text{and } d_{(100)} = 3.04 \times 10^{-8} \text{ cm.}$$

Putting this value of  $d$  in  $\lambda = 2d \sin \theta$ , and also the value of  $\lambda$  for the palladium ray, we get :

$$0.584 \times 10^{-8} = 2 \times 3.04 \times 10^{-8} \sin \theta_{(100)},$$

from which we find that

$$\sin \theta_{(100)} = 0.0950, \text{ and } \theta_{(100)} = 5^{\circ}4'.$$

The actual glancing angle observed from the  $r = \{100\}$  faces was

$5^{\circ}35'$  as above stated. The correspondence between the actual and calculated glancing angles is so close that there is every reason for believing the assumption of a four-molecule rhombohedral cell to be correct.

On acting similarly for the other faces of calcite, of the forms  $\{110\}$ , the inverse obtuse rhombohedron usually lettered  $e$ ,  $\{111\}$ , the basal pinakoid  $c$ , and  $\{2\bar{1}\bar{1}\}$ , the hexagonal first order prism  $m$ , on the four-molecule cell basis we obtain the calculated angles of reflection  $8^{\circ}63'$ ,  $5^{\circ}92'$ , and  $11^{\circ}59'$ . The observed glancing angles from these forms were  $8^{\circ}70'$ ,  $5^{\circ}77'$ , and  $11^{\circ}65'$ , thus confirming most satisfactorily that the space-lattice was correctly diagnosed.

The arrangement of the individual atoms of the  $\text{CaCO}_3$  molecule about each point of the lattice was next ascertained by consideration of the special features of the spectra from each face. It was found to be

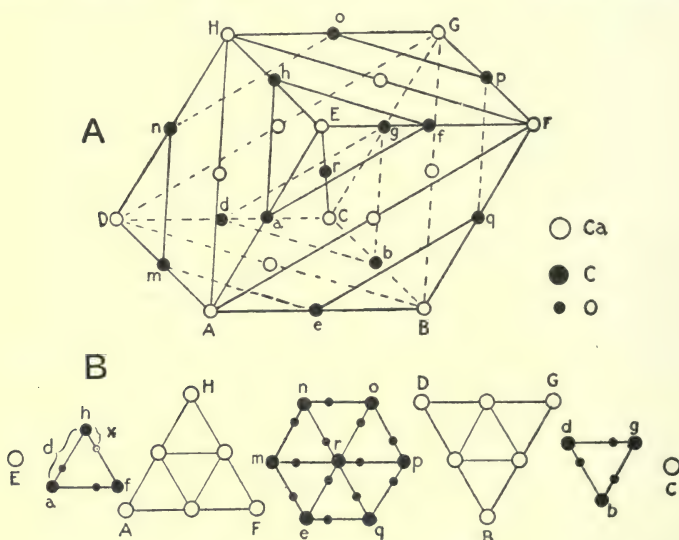


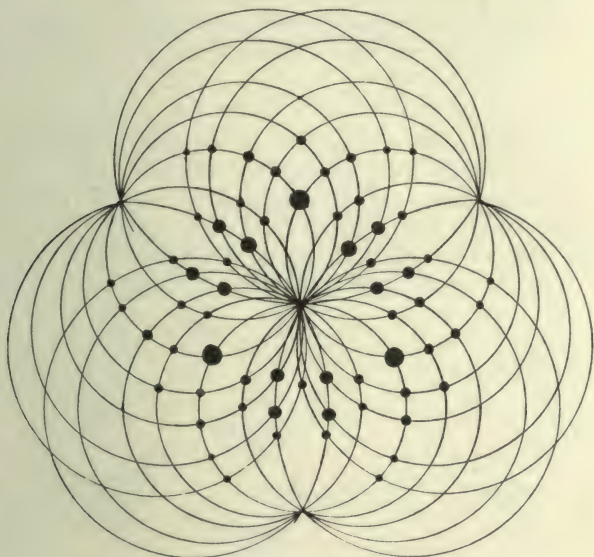
FIG. 560.—The Structure of Calcite.

that shown in Fig. 560. At A only the calcium (capital letters) and carbon (small letters) atoms are shown; in B the oxygen atoms are also shown (unlettered), in the various layers parallel to the basal plane (111) and perpendicular to the trigonal axis. The planes are evenly and equally spaced, and contain alternately calcium atoms and groups of the composition  $\text{CO}_3$ . The spacing  $d_{(111)}$  is the distance between two similar planes (of Ca or  $\text{CO}_3$ ). The diagram of a Laue radiogram for calcite, taken by Sir William Bragg with a plate cut perpendicular to the trigonal and optic axis, is also reproduced in Fig. 561. An excellent model is illustrated at *b* and *c* in Fig. 584*c* on page 717.

The Bragg structure for calcite above described has been shown by W. Voigt (*loc. cit.*) to correspond to Sohncke's type No. 21 (Fig. 493 on page 609), the compound rhombohedron system. Second kind coincidence



movements are not required to account for the structure. According to R. W. G. Wyckoff<sup>1</sup> it is the special case (*g*) of the space-group  $D_{3d}^6$  of Schönflies, of which  $\Gamma_{rh}$  is the underlying space-lattice. Wyckoff has also emphasised the existence of  $\text{CO}_3$  groups as definite entities in the structure of calcite, and also in the other carbonates of the calcite group, the triads of oxygen atoms being at a constant distance of  $1.22 \times 10^{-8}$  cm. from the carbon atom throughout the series, while all other atomic distances vary from member to member of the series. The calcium, oxygen, and carbon atoms all follow this type 21. It is interesting that Voigt also shows that the crystals of the elements bismuth, antimony (see also page 687), and arsenic also conform to Sohncke's system No. 21.



• FIG. 561.—Laue Radiogram of Calcite.

The isomorphous carbonates  $\text{FeCO}_3$  and  $\text{MnCO}_3$  are similarly constructed, as are also dolomite  $(\text{CaMg})\text{CO}_3$  and sodium nitrate  $\text{NaNO}_3$ , which latter is well known greatly to resemble calcite. In the cases of  $\text{FeCO}_3$  and  $\text{MnCO}_3$  direct proof is given of the equal effect of similar atomic weight; for the iron planes (atomic weight 56) or the manganese planes (55) are found to balance the  $\text{CO}_3$  ( $12 + 48 = 60$ ) planes, the first order spectrum being extinguished. The accompanying diagram, Fig. 562, records the intensity of the first order reflection from the basal plane of all these five substances; it will clearly be perceived how the fall of intensity accompanies the decrease of the mass difference between the two series of layers, and how when the difference reaches practically zero the first order spectrum disappears altogether.

**Quartz.**—A Laue radiogram of quartz,  $\text{SiO}_2$ , has already been given

<sup>1</sup> *Amer. Journ. of Science*, 1920, 50, 317.

in Fig. 535, taken with a plate cut perpendicularly to the trigonal and optic axis. This well-known and important mineral of class 18 (see page 354) has proved more difficult than the substances previously dealt with, as regards the structural interpretation of the X-ray spectra reflected from its principal facial planes. Calcite has been interpreted in the last section on the basis of a rhombohedral space-lattice, No. 7 (Fig. 462, page 586), but quartz is constructed on the basis of the trigonal

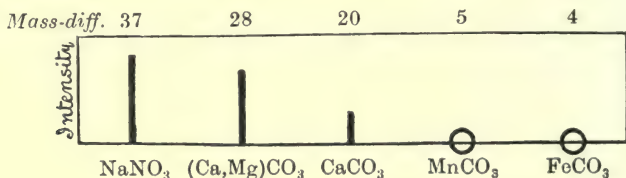


FIG. 562.

60°-prism space-lattice No. 6 (Fig. 457 or 458, page 584), for the spectra are best interpreted on this assumption and all other considerations concur. The usual hexagonal prism of quartz,  $m = \{2\bar{1}\bar{1}\}$  (Figs. 321 and 322, page 363) affords reflections of first order spectra from its faces at the smallest angle observed from any of the facial forms, namely,  $7^\circ.8$ , whereas the rhombohedral faces  $\{100\}$  give the larger angle of  $10^\circ$  for the

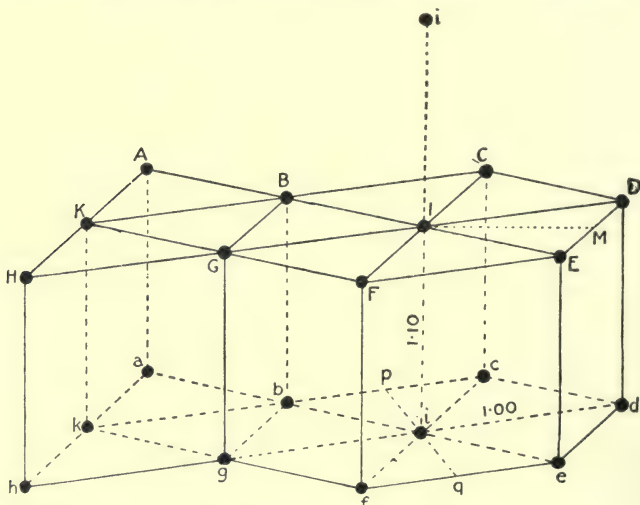


FIG. 563.—The Structure of Quartz.

first spectra, and the basal plane  $\{111\}$  at  $18^\circ.5$ . In calcite, on the contrary, the first order reflection from  $\{2\bar{1}\bar{1}\}$  occurs at  $24^\circ$ , and the first order reflection from  $\{100\}$  and  $\{111\}$  at  $11^\circ$  and  $11^\circ.2$ . Hence, in calcite the rhombohedron is the principal form, while in quartz the hexagonal prism is the chief form; the space-lattice elementary cells are conse-

quently probably rhombohedral and prismatic respectively. The prismatic structure of quartz is, therefore, in all likelihood, that indicated in Fig. 563.

The axial ratio  $a : c = 1 : 1.10$ , and  $a = 10$  and  $c = 11$ . The volume of each prism (that is, associated with each point of the space-lattice) is  $\frac{\sqrt{3}a^2c}{2}$ . From the data afforded by the first order spectrum and the

density of quartz 2.65, the mass contained in unit cell of the lattice works out as  $2.94 \times 10^{-22}$  grammes. Now the mass of one molecule  $\text{SiO}_2$  is :

$$(28.3 + 32) \times 1.64 \times 10^{-24} \text{ grammes} = 0.99 \times 10^{-22} \text{ grammes.}$$

This value is practically exactly one-third of that for the unit cell, so that in the latter there must be three molecules of  $\text{SiO}_2$ , that is,  $3\text{SiO}_2$  associated with each point of the lattice. Assuming this to be correct, and then working backwards and calculating the glancing angles of the first order spectrum from each of the principal faces as was done in the case of calcite, a remarkably close agreement is found between these values and the experimental ones, except in the case of the basal plane  $c$  (111) or (0001), for which the value of the observed angle is three times the calculated angle, and the spacing of these planes is three times smaller than that of the underlying lattice.

From this Sir William Bragg concludes that three hexagonal space-lattices interpenetrate, one being derived from the other by a rotation of  $60^\circ$  about, and translation for  $c/3$  along, the

direction of the vertical axis  $c$  (of Bravais-Millerian notation), the trigonal axis of the structure. This axis has consequently the points arranged spirally around it, and the spiral may be either right or left handed, corresponding to the two varieties of quartz. Such a structure would perfectly fit the observed character of the X-ray spectra. In Fig. 564 the general arrangement of the atoms is represented, the black discs being representative of silicon atoms and the white ones of oxygen atoms. Three digonal axes intersect in the trigonal axis, and a silicon atom lies on each digonal axis.

It will be obvious that such a structure for quartz would be in accord

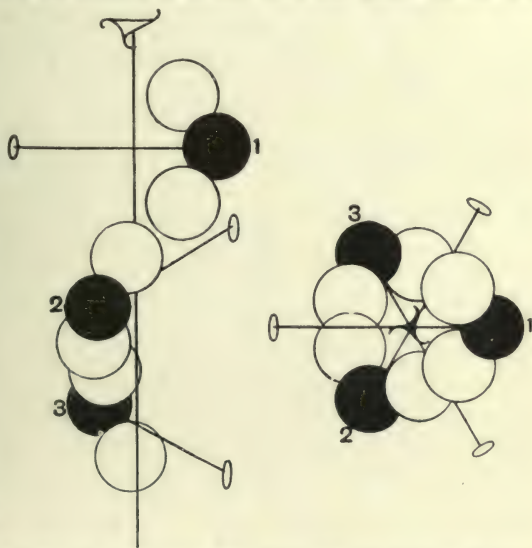


FIG. 564.—Arrangement of Silicon and Oxygen Atoms in Quartz.



with the general properties of this particularly interesting and important mineral. Sir William Bragg foreshadows further exact details as to the actual dimensional positions of the atoms.

According to W. Voigt (*loc. cit.*) the oxygen atoms in quartz are grouped according to Sohncke's types Nos. 18 and 19 (Fig. 491 on page 609), the right and left compound 3-point screw systems, and the silicon atoms in accordance with the specialisation of those systems which occurs when the initial atom lies on a lateral axis.

**Corundum (Ruby) and Hæmatite.**—The ruby,  $\text{Al}_2\text{O}_3$ , and hæmatite,  $\text{Fe}_2\text{O}_3$ , belonging to the calcite class 21 of the trigonal system, have also

been investigated by Sir W. H. Bragg. Corundum crystals, as already described on page 345, are known as sapphire when blue, and as ruby when red, the colour being due to ferric oxide. A typical sapphire is shown (by the kindness of Sir Henry Miers) in Fig. 564a, and a characteristic ruby in Fig. 564b.

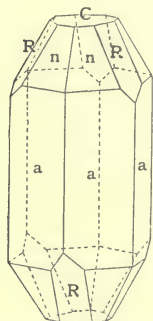


FIG. 564a.—Sapphire.

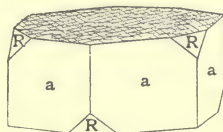


FIG. 564b.—Ruby.

The faces marked *a* are those of the second order hexagonal prism  $\{10\bar{1}\}$ , those labelled *R* form the primary first order rhombohedron  $\{100\}$ , those lettered *n* are faces of the second order hexagonal bipyramid  $\{31\bar{1}\}$ , and those marked *C* are the faces of the basal pinakoid  $\{111\}$ . The habits shown are characteristic of the two gemstones, and the cross-hatching on the basal plane of the ruby represents the triangular striations due to lamellar twinning on the rhombohedron *R*, which are almost always present on the tabular crystals of this gem.

The cases of corundum and hæmatite are not so simple as those of calcite, and extensive use has been made of the principle, which the large volume of work on X-rays and crystals now carried out appears to have fully substantiated, that the amplitude of a wave of X-rays reflected or diffracted by an atom is proportional to the atomic weight of that atom. The principle enables the general case to be attacked in which planes that are not of identical nature are spaced in accordance with some more complicated law.

The intensity of reflection is proportional to the square of the amplitude. Hence, the intensity of reflection at any plane of atoms of the crystal structure is afforded by the square of the mass represented by the chemical composition (sum of atomic weights of the atoms in the plane). Thus in calcite, for instance, the planes of atoms parallel to the basal plane (111) are alternately composed of only calcium atoms (at. wt. 40) and groups of atoms  $\text{CO}_3$  (sum of at. wts.  $12 + 48 = 60$ ); the intensity of reflection from these successively alternating basal planes of atoms will, therefore, be represented by  $(40)^2$  and  $(60)^2$ .

Let the distance between the two planes of one kind be *d*, and that

between a plane of one kind and a plane of the other kind be  $x$ . Each pair of planes (one of each kind) sends off two wave-trains of the same length but of different phase and amplitude. The phase difference  $\theta$  is given by :

$\frac{\theta}{2\pi} = \frac{x}{d}$  (for 1st spectrum), or  $\frac{2x}{d}$  (for 2nd spectrum), or  $\frac{3x}{d}$  (for 3rd spectrum), etc.

The amplitudes are proportional to the masses  $M_1$  and  $M_2$ , and the amplitudes of the resultant wave  $R$  is (by a well-known device) the geometrical resultant of two vectors  $M_1$  and  $M_2$  making an angle  $\theta$  with each other, that is,

$$R^2 = M_1^2 + M_2^2 + 2M_1M_2 \cos \theta.$$

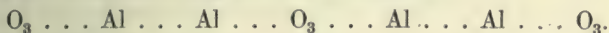
If now  $I_1, I_2, I_3, I_4, I_5$ , etc., be the intensities when  $x = 0$ , and  $I_1', I_2', I_3', I_4', I_5'$ , etc., the intensities when  $x$  has an actual value, then

$$I_1' = I_1 \left( \frac{M_1^2 + M_2^2 + 2M_1M_2 \cos \frac{2\pi x}{d}}{(M_1 + M_2)^2} \right),$$

$$I_2' = I_2 \left( \frac{M_1^2 + M_2^2 + 2M_1M_2 \cos \frac{4\pi x}{d}}{(M_1 + M_2)^2} \right), \text{ etc.}$$

This general formula enables the calculation of the theoretical intensities of the various orders of reflection at any structural plane of atoms to be made. In the case of calcite, for instance, the ratio  $x : d$  of  $B$  in Fig. 560, page 682, is given exactly as 0.26.

This principle has proved very useful in the complicated cases of ruby and hæmatite. The structure arrived at is obtained if we suppose the three oxygen atoms to be arranged as they are in calcite (Fig. 560), the carbon atoms of calcite to be removed, and the calcium atoms to be replaced each by two atoms of aluminium arranged like a dumb-bell parallel to the axis  $c$ . The ratio  $x/d$  again determines the position of the oxygen atoms, and proves to be  $1/2$ . The second variable is the distance between the two aluminium atoms of each dumb-bell pair. The (111) planes, therefore, have the following order of succession :



As the second and third spectra are stronger than the first spectrum, it is probable that the distance  $Al \dots Al$  is somewhat smaller than the distance  $Al \dots O_3$ .

According to W. Voigt (*loc. cit.*) this hæmatite and ruby structure corresponds, like calcite, to Sohncke's system No. 21 (Fig. 493 on page 609). The oxygen atoms are as in calcite, the carbon atoms of the latter are eliminated, and the calcium atoms are replaced by an axial pair of iron or aluminium atoms.

**Antimony.**—The structure of the crystals of the element antimony has been studied by R. W. James and N. Tunstall<sup>1</sup> in the laboratory

<sup>1</sup> *Phil. Mag.*, 1920, 40, 233.

of Prof. W. L. Bragg. The crystals belong to the ditrigonal scalenohedral class 21 of the trigonal system, like calcite, the habit being rhombohedral like the latter. The rhombohedral angle  $(100) : (010)$  is  $92^{\circ} 53'$  and the Millerian rhombohedral axial angle  $a$  is  $86^{\circ} 58'$  (Laspeyres), the rhombohedron being thus only a slightly deformed cube. The main cleavage is parallel to the basal pinakoid  $c \{111\}$ , with a less perfect one parallel to the obtuse negative rhombohedron  $e \{110\}$ . The structure is found to consist of two interpenetrating rhombohedral space-lattices No. 7, but with a point in the centre of each face. The atoms of the second lattice do not lie at the unoccupied corners of the rhombohedral cells of the first lattice, but are displaced therefrom along the diagonals which are parallel to the trigonal axis, by a distance 0.074 of the length of the diagonal of one of the eight small rhombohedra into which the main rhombohedron may be divided. The planes containing the atoms parallel  $(111)$  occur in pairs, two close together, then an interspace, then two close together again, those belonging to one lattice dividing the distance between those of the other in the ratio 0.389 to 0.611. The main cleavage is parallel to these pairs of planes. The closest distance of approach of two Sb atoms is  $2.87 \times 10^{-8}$  cm., and Prof. W. L. Bragg takes this as the atomic diameter of antimony (see page 713).

**Carborundum**, silicon carbide,  $\text{SiC}$ , has been studied by C. L. Burdick and E. A. Owen.<sup>1</sup> This exceedingly hard yet comparatively light substance, specific gravity 3.123, obtained by the action of the high-temperature electric arc on coke and quartz, forms crystals belonging to the trigonal system, the class having been a matter of some controversy. The crystals are usually hexagonal plates parallel to the trigonal basal plane  $\{111\}$ , with numerous modifying edge-faces, chiefly the second order prism  $\{10\bar{1}\}$  and several rhombohedra; often only three of the rhombohedral faces, that is, a trigonal pyramid, are developed in the case of any one rhombohedron, so that Becke has concluded that the class is the ditrigonal pyramidal, class 20, a conclusion confirmed by the etch-figures. Negri<sup>2</sup> has shown that there are two types, tabular and pyramidal, with intermediate combinations, and gives the elements as  $a : c = 1 : 1.2266$ , and  $a$  (the angle between the edges of the primary rhombohedron) as  $89^{\circ} 57'$ . The elementary rhombohedron is thus practically a cube, there being only three minutes difference from  $90^{\circ}$  (probably the special case referred to on page 342). It is found by Burdick and Owen that the structure is, in fact, very like that of the diamond, the carbon and silicon atoms being each arranged on face-centred rhombohedral (practically cubic) lattices. Reproductions of a Laue photograph by Owen, and also of the diagram of spots deduced from this radiogram, are given at A and B in Fig. 565. In the planes of the first and second order hexagonal prisms,  $\{2\bar{1}\bar{1}\}$  and  $\{10\bar{1}\}$ , the carbon and silicon atoms lie in the same planes, and in the direction of the principal axis the atoms of the two elements alternate, there being no lateral displacement between the two kinds of atoms with respect to

<sup>1</sup> *Journ. Amer. Chem. Soc.*, 1918, 40, 1749; also see E. A. Owen, *Proc. Roy. Soc., A*, 1918, 94, 340.

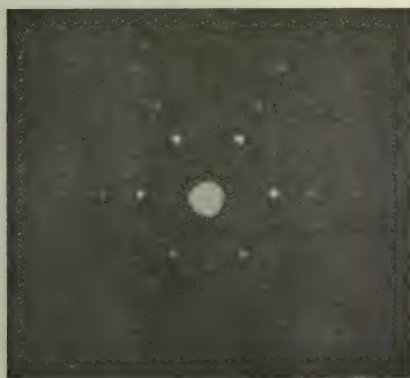
<sup>2</sup> *Rivista d. min. e crist. ital.*, Padua, 1903, 29, 33.



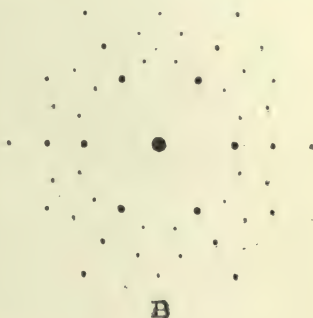
this axis. The distance of the carbon planes from the silicon planes in the direction of the axis is 0.36 of the distance between two consecutive carbon or silicon planes.

The structure can be derived from that of the diamond by replacing the carbon atoms of one of the two interpenetrating face-centred cubic lattices of the diamond by a similar lattice of silicon atoms, shortening one trigonal axis by 0.15 per cent., and displacing the atoms of one lattice from a position 0.25 to one of 0.36 of the distance between successive planes of the other lattice, in the direction of the shortened axis.

**Cæsium Dichloriodide**,  $\text{CsCl}_2\text{I}$ , has been studied by Wyckoff<sup>1</sup> and found to be rhombohedral, with a structure resembling that of rock-salt compressed along a trigonal axis until the  $90^\circ$  becomes  $80^\circ 12'$ . The



A



B

FIG. 565.—Laue X-radiogram of Carborundum.

absolute length of this axis is  $6.06 \times 10^{-8}$  cm. The atoms of cæsium and iodine are arranged at alternate corners, and an atom of chlorine is situated on the axis at 0.62 of its length from a cæsium or iodine atom. The case is interesting, as the atomic weights of cæsium (132) and iodine (127) are so nearly equal that the reflecting powers of the alternate horizontal strata containing the atoms of these elements are practically the same.

**Graphite.—The Method of Debye and Scherrer.**—As the result of a remarkable research P. Debye and P. Scherrer<sup>2</sup> obtained X-ray interference figures by compressing the crystalline powder of the graphitic form of carbon into a small rod, placing the latter in the axis of a cylindrical sensitive film, and subjecting the rod to the influence of “monochromatic” X-rays. On developing the film characteristic curves were shown, the result of interference phenomena caused by the structure of the minute crystals. This experiment with graphite inaugurated a third method of X-ray analysis.

<sup>1</sup> *Journ. Amer. Chem. Soc.*, 1920, 42, 1100.

<sup>2</sup> *Nach. Ges. Wiss.*, Göttingen, 1916, p. 1; *Phys. Zeitschr.*, 1916, 17, 277; 1917, 18, 291.

The principle of this remarkable new method appears to be as follows: If a fine monochromatic beam of X-rays be caused to impinge on a crystal face at the correct glancing angle  $\theta_1$ , for the first order reflection, and the reflected rays be received on a narrow sensitive photographic film curved into a semicircle of which the crystal is the centre, the film on development will show a much over-exposed line where the direct beam had struck it, and another line at an angular distance from this first line of  $2\theta_1$ , due to the cumulative reflection from planes of atoms parallel to the face of the crystal under investigation. When the glancing angle is increased to  $\theta_2$  corresponding to the second order reflection a third line is produced at the angular position  $2\theta_2$ , and so on for the successive orders. If now the crystal plate be replaced by the finely powdered crystal substance and an exposure be made without setting to any specific glancing angle, there will be a considerable number of minute crystals having the first of the above orientations, there will, in fact, be a hollow cone of such particles, the angle of the cone being  $4\theta_1$ , and the semicircular film will show two lines (one on each side) corresponding. Similarly, there will be another cone of numerous crystallites having the second orientation, which will afford two further corresponding lines, and so on for the other orders of X-ray spectra. The distances of the various lines on each side from the over-exposed central line depend on four factors, namely, the wave-length of the "monochromatic" X-radiation, the grating (spacing) distance  $d$  of the planes of atoms from each other, the order of reflection, and the radius of the circular film.

It is interesting that all the faces of a form combine to give the same line on the film. Indeed, the chances of crystallites having the correct orientation are multiplied in accordance with the number of faces which go to make up a form, and the intensity of the line is also proportionately increased. The crystal powder need only be very small in quantity, 0.005 gramme in weight, or even less, and should be contained in a thin-walled glass tube, or one of celluloid or collodion. It is best of all pressed into a cylindrical rod, preferably coated with collodion to prevent disintegration. A rod 10 mm. long and 1 mm. in diameter suffices. The film is used also in cylindrical form, with the axis of the cylinder arranged perpendicularly to the incident beam. The beam of X-rays should fall on the middle of the rod.

The apparatus is shown in elevation in Fig. 565*a*, and in Fig. 565*b* is given a reproduction of one of the actual photographs. The X-rays are delivered into the cylindrical camera through a brass tube, seen on the left, 9 cm. long and of 1.5 mm. bore. The rod of substance is suspended centrally from a circle-plate, with means of adjustment exactly to the axis of the sensitive film-cylinder. The film itself is confined between the outer brass cylinder forming the camera and a blackened cardboard inner cylinder of slightly smaller diameter, paper being pervious to X-rays. A monochromatic X-ray tube, with copper anticathode, giving very intensely the  $\alpha$ -line of the K-series, is most effective, and the stronger of the pair, in the case of each of the double-curved lines shown in Fig. 565*b*, is due to this  $\alpha$ -radiation, the weaker being due to the  $\beta$ -line of the K-radiation. The curves are of the fourth degree.

If the reflection angle be  $\theta$  for the spacing  $d$ , the cone of reflected rays is  $2\theta$ . For a cubic crystal, if  $a$  be the length of the cube edges (lattice constant),  $\lambda$  the wave-

length of the X-rays, and  $hkl$  the Millerian indices of the facial plane at which reflection occurs; then

$$\sin^2 \frac{\theta}{2} = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2).$$

The result for  $\sin^2 \frac{\theta}{2}$  works out to be a whole number. If the crystal be not cubic the calculation is more complicated, the lengths of the sides of the elementary parallelepipedon of the lattice and their angles of inclination requiring to be taken into consideration.

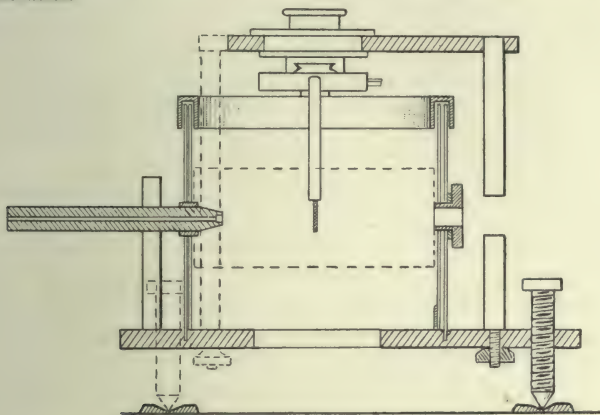


FIG. 565a.—The Apparatus of Debye and Scherrer.

It is interesting that with this apparatus not only powdered crystals but also colloidal particles of the finest character have been investigated. Scherrer,<sup>1</sup> for instance, has found that the finest precipitated gold consists of crystal-particles having the same centred-face-cube structure as ordinary large gold crystals. Fig. 565b was actually obtained from such a specimen—a fine light-brown powder contained in

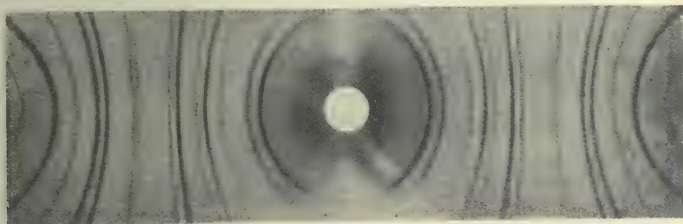


FIG. 565b.—A typical Debye and Scherrer X-radiogram.

a collodion tubelet. The film showed 19 interference lines. Another specimen of so-called colloidal gold proved to consist of particles only  $1.86 \times 10^{-7}$  cm. in diameter, so that only 5 cube-lattice edge-lengths were contained in each particle; yet it gave a clear interference photograph little inferior to Fig. 565b. Silver and silica in their finest so-called colloidal forms also gave figures proving them to be crystalline, the former completely so, with a face-centred cubic lattice, but the latter only partially. Gelatine, however, showed no trace of crystallisation.

The crystal form indicated for graphite is trigonal, rhombohedral, the absolute dimensions of the space-lattice rhombohedral cell being

<sup>1</sup> Zsigmondy's *Kolloidchemie*, 3rd edition, p. 387.



$a=b=c=4.48 \times 10^{-8}$  cm., and  $d_{(111)}=3.41 \times 10^{-8}$  cm. This latter (the spacing of the (111) planes) was measured also by Sir W. H. Bragg by his ordinary method and found to be  $3.42 \times 10^{-8}$  cm. This close agreement with the result of Debye and Scherrer would appear to confirm the work of the latter and the value of their singular new method. They have also experimented with ordinary amorphous carbon, and found its fine particles to have the same rhombohedral crystal structure as graphite, and conclude, therefore, that there are only two true varieties of carbon, diamond and graphite, and that in diamond the four valencies are arranged tetrahedrally, while in graphite there are three principal valencies arranged at  $120^\circ$  from each other in a plane, and a fourth feebler valency placed perpendicularly to that plane. These two structures thus agree with the two kinds of chemical properties exhibited by the fatty and aromatic carbon compounds.

This structure for graphite corresponds, according to W. Voigt (*loc. cit.*), to the special case of Sohncke's Nos. 22 and 23 (Fig. 494 on page 610), the right and left alternating 3-point screw systems, in which enantiomorphism disappears, the hexagons lying parallelwise. The carbon atoms have three of their valencies turned towards their neighbours, but the fourth at right angles to the plane of those three.

This remarkable method of Debye thus enables the structure to be determined even in a confused aggregate of crystals. Indeed the authors claim for it that it also enables the size of liquid molecules to be determined, and as the result of experiments with benzene they state that the molecule of this important substance has the form of a hexagonal tablet, the edge of the regular hexagon having the absolute length  $6.02 \times 10^{-8}$  cm., and the thickness of the tablet being about  $1.19 \times 10^{-8}$  cm. This result fulfils chemical expectations in a manner which is eminently satisfactory, provided the interpretation of the experiments be fully substantiated by further work.

The method appears to have been quite independently discovered by A. W. Hull,<sup>1</sup> who passed a narrow beam of X-rays through a disordered mass of small crystals of aluminium, iron, steel, silicon, magnesium, graphite, and diamond, and in each case photographed the diffraction pattern obtained. The substance was powdered as finely as possible to ensure random average orientation of the particles of the crystals, and the "monochromatism" of the X-rays was rendered more perfect by filtering them through screens capable of absorbing undesirable wavelengths. Hull finds a molybdenum anticathode, used with a screen of zirconium or zircon, very effective. Hull's results for graphite, using a molybdenum anticathode, led him to a hexagonal structure, a kind of bee-cell arrangement of 4 simple triangular No. 6 lattices, each of side  $2.47$  and  $6.80 \times 10^{-8}$  cm. height, the atoms of the third lattice being directly above those of the first at a distance of half the height of the prism, and those of the second and fourth being above the centres of alternate triangles of the first, at distances  $\frac{1}{4}$ th and  $\frac{3}{4}$ ths of the height of the prism respectively.

<sup>1</sup> *Phys. Rev.*, 1917, 10, 661; also *Science*, 1920, 52, 227.

It is highly satisfactory that Hull, by use of his method, confirms absolutely Bragg's results for the diamond. For silicon he finds a similar result, the cube edges being  $5.43 \times 10^{-8}$  cm., which is almost identical with the value 5.46 which has been obtained by Debye and Scherrer.

Hull has also used his method to determine the structure of crystals of sodium, iron, aluminium, and nickel. Sodium, iron, and nickel have centred cube lattices, the lengths of their cube edges being 4.30, 2.86, and  $2.76 \times 10^{-8}$  cm. Aluminium has a face-centred cube lattice, with cube edge of  $4.05 \times 10^{-8}$  cm. Debye and Scherrer obtained  $4.07 \times 10^{-8}$  cm. Hull has more recently (1920) found that calcium, palladium, platinum, and iridium have a face-centred cubic structure, and that titanium, chromium, tungsten, and tantalum are centred cubic.

**Hexagonal Crystals.**—The structure of metallic **magnesium** has been investigated by A. W. Hull.<sup>1</sup> The crystals of this metal were first obtained by Dumas, by sublimation in an atmosphere of hydrogen, and were measured by Des Cloizeaux and found to be hexagonal prisms  $\{10\bar{1}0\}$  terminated by the basal plane  $\{0001\}$  and the primary pyramid  $\{10\bar{1}1\}$ . Similarly constituted and very perfect and beautiful crystals were obtained more recently by Bamberger in the separation of argon from nitrogen by leading the gases over glowing magnesium. Hull now finds this structure confirmed by X-ray analysis both by the Laue method with good crystals and by his modification of the method of Debye and Scherrer, using for the latter method magnesium powder. The space-lattice is that of the triangular prism No. 6 (Fig. 457), there being two sets of such prisms, so arranged that the Mg atoms of one set are in the centre of the prisms of the other. The dimensions are  $a = 3.22$  and  $c = 5.23 \times 10^{-8}$  cm. The arrangement is that of Barlow's closely packed hexagonal system of spheres, slightly deformed. This result has been confirmed by H. Bohlin,<sup>2</sup> who also used the Debye and Scherrer method, but with the powdered crystalline magnesium compressed to form a cylindrical arc-shaped surface, the interference lines being thereby materially sharpened. Hull has more recently (1920) found that zinc, cadmium, and ruthenium have a closely packed hexagonal structure, the two former being elongated 14 and 16 per cent., and ruthenium contracted 3 per cent., along the hexagonal axis.

**Zinc Oxide.**—The structure of crystals of ZnO has been studied by W. L. Bragg.<sup>3</sup> They belong to the dihexagonal pyramidal class 26 of the hexagonal system, the axial ratio being  $a : c = 1 : 1.6077$  (Traube). They cleave perfectly parallel to the first order hexagonal prism  $m \{10\bar{1}0\}$ , and less perfectly parallel to the basal plane  $c \{0001\}$ . The zinc atoms are found to be arranged on two hexagonal space-lattices (No. 6), their centres corresponding closely with those of a set of equal spheres in hexagonal close packing, the slight difference being a contraction (1.608 instead of 1.632) along the hexagonal axis. The oxygen atoms appear to lie on the same two hexagonal space-lattices, being removed from the zinc atoms by a translation parallel to the hexagonal  $c$ -axis, such as

<sup>1</sup> *Nat. Acad. Sci. Proc.*, 1917, 3, 470.

<sup>2</sup> *Ann. der Physik.*, 1920, 61, 421.

<sup>3</sup> *Phil. Mag.*, 1920, 39, 647.

brings every O atom into the centre of four Zn atoms arranged at the corners of an almost regular tetrahedron. Parallel to the basal plane (0001) the Zn and O atoms are arranged on alternate planes, the O atoms dividing the distance between the Zn planes in the ratio 1 : 3, which agrees with the polar nature of the *c*-axis in accordance with class 26 symmetry. The smaller distance in absolute measure is 0.64 Å. The first order hexagonal prism faces  $m\{10\bar{1}0\}$  have planes containing an equal number of Zn and O atoms, spaced alternately at 0.93 and 1.87 Å distances.

**Zinc Sulphide, Wurtzite.**—This hexagonal variety of ZnS, and also **Greenockite**, CdS, which also belong to class 26, show analogous structures, according to Prof. Bragg, and are thus isomorphous and isostructural.

**Ice.**—F. Rinne<sup>1</sup> has obtained some excellent Laue radiograms of ice crystals parallel to the basal plane (0001). They agree with hexagonal rather than trigonal (as assumed by von Groth) symmetry, with an axial ratio of  $a : c = 1 : 1.678$ .

**Tetragonal Crystals—Tin.**—The method of Debye and Scherrer is particularly suitable for metals and micro-crystalline substances in general. It has, therefore, been employed by A. J. Byl and N. H. Kolkmeier<sup>2</sup> to investigate the structure of the two varieties of tin—grey tin and ordinary white tin. They used a Röntgen tube with copper anticathode. The X-rays left the tube by an aluminium window 0.02 mm. thick, and then passed through an aperture 2 mm. diameter in a lead screen 34 mm. thick. This narrow and slightly converging beam then entered a cylindrical camera of 27.3 mm. radius, the material to be investigated being placed in the axis of the camera, in the form of a bar of 2 mm. diameter. One such bar was filed from a larger bar of white beaten tin, and another was made by compressing grey tin into bar form. A photographic sensitive film of 0.2 mm. thickness was stretched along the wall of the camera and pressed against it by springs. The intensity of the interference lines produced in the two cases was estimated in five degrees of strength, and a drawing prepared in which the lines appear like a spectrum, their thickness representing their intensity. They represent the places of the interference maxima in a plane perpendicular to the axis of the bar.

The results for grey tin<sup>3</sup> indicate that this variety of tin is crystalline, and that the crystals are cubic. There appear to be eight atoms to a cube, which corresponds to the structure of the diamond. The data

<sup>1</sup> *Ber. Verh. Sächs. Ges. Wiss.*, 1917, 69, 57.

<sup>2</sup> *Proc. Kon. Akad. van Wetenschappen*, Amsterdam, 1918, 21, 405 and 494.

<sup>3</sup> It will be remembered that "grey tin" is the remarkable powdery form of tin, to which the metal crumbles when exposed to great cold; tin organ-pipes disintegrate in this manner sometimes in very cold winters, and the occurrence has become industrially known as "tin pest." As the temperature of transition is above 0° C., namely 18°, tin is ordinarily in the metastable condition, except on warm days. The change from white to grey tin occurs most rapidly at -48° C. The "pest" is curiously communicated rapidly to sound tin by contact with a piece of tin already in process of undergoing the change. On the other hand, on heating, ordinary tetragonal white tin passes into a third rhombic modification at a temperature between 170° and 200° C. The metal melts at 232° C.



employed was : atomic weight of tin = 119 ; specific gravity at  $18^\circ = 5.751$  ; wave-length of the copper radiation used,  $\text{Cu}_{K\alpha} = 1.541 \times 10^{-8}$  cm. ; Avogadro's number =  $6.06 \times 10^{23}$ . The edge of the elementary cube works out to be  $6.46 \times 10^{-8}$  cm. The distance of the two nearest atoms is  $2.80 \times 10^{-8}$  cm. This structure is not only like that of the diamond, but is also possessed by silicon, which has likewise been investigated.

Tetravalency is thus obviously indicated for grey tin, as for diamond carbon.

White tin, the ordinary form of metallic tin, crystals of which were investigated by Miller in 1843 and found to be tetragonal holohedral, with the axial ratio  $a : c = 1 : 0.3857$ , and which has a specific gravity at  $18^\circ$  of 7.285, afforded interference lines agreeing with Miller's results, and with the supposition that there are three atoms to a cell of the tetragonal space-lattice. This agrees with a structure in which there are tin atoms at the corners of the tetragonal cells and at the centres of the prism faces, but not in the centres of the basal pinakoid faces. Fig. 566 will render the structure clear.

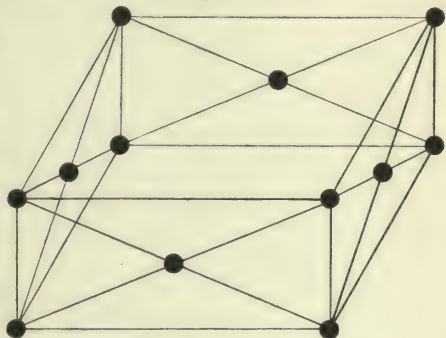


FIG. 566.—The Structure of White Tin.

The dimensions of the cell are :  $a = 5.84 \times 10^{-8}$  cm. and  $c = 0.406a = 2.37 \times 10^{-8}$  cm. There are alternating equidistant layers at the distance  $1.19 \times 10^{-8}$  cm. The first layer has a netting of squares with the side  $5.84 \times 10^{-8}$  cm., and the next layer a netting of squares with  $4.13 \times 10^{-8}$  cm. side, these latter squares being just above squares inscribed symmetrically within the squares of the first layer.

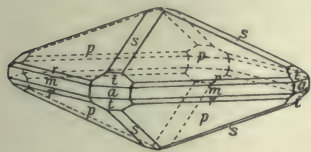


FIG. 567.  
Miller's Setting for White Tin.

This elementary cell would not correspond to Miller's choice of parametral plane, but would convert his primary pyramid  $p = \{111\}$  (which is a very flat one) into  $\{403\}$ , and his forms  $m = \{110\}$ ,  $a = \{100\}$ , and  $s = \{101\}$  would become respectively  $\{100\}$ ,  $\{110\}$ , and  $\{223\}$ . Fig. 567 represents Miller's setting. The new setting would require it to be rotated  $45^\circ$  about the vertical axis.

A. W. Hull<sup>1</sup> has found that indium atoms are arranged in a tetragonal structure, like a face-centred cube, but elongated 6 per cent. along the tetragonal axis.

Crystals of the minerals of the **Zircon Group**, namely, zircon  $\text{ZrSiO}_4$  or  $\text{ZrO}_2 \cdot \text{SiO}_2$ , rutile  $\text{TiO}_2$ , cassiterite  $\text{SnO}_2$ , and thorite  $\text{ThSiO}_4$ , have been investigated by Vegard.<sup>2</sup> He concludes that in zircon the silicon and

<sup>1</sup> *Science*, 1920, 52, 227.

<sup>2</sup> *Phil. Mag.*, 1916, 32, 68.

zirconium atoms are arranged in tetragonal lattices of the diamond type. When both the zirconium and the silicon are replaced by the same element titanium or tin, the lattice becomes a prism-centred one, space-lattice No. 5 (Fig. 456, page 583), as regards the metallic atoms. The oxygen atoms also have a tetragonal arrangement. In the elementary cell there is one-eighth of a molecule, that is, there is just one molecule in the rectangular prism having the sides  $2d_{(100)}$ ,  $2d_{(100)}$ ,  $2d_{(001)}$ . The elementary lattice is thus a prism with one atom in each corner, the side of the square base being  $a$  and the height  $c$ , that is,  $d_{(100)}=a$ , and  $d_{(001)}=c$ . Thus in the cell  $2d_{(100)} \cdot 2d_{(100)} \cdot 2d_{(001)}$  there are one zirconium atom, one silicon atom, and four oxygen atoms. The distance of the zirconium atom from either of the two oxygen atoms associated with it is twice the corresponding distance between a silicon atom and its two oxygen satellites, a fact probably due to the greater

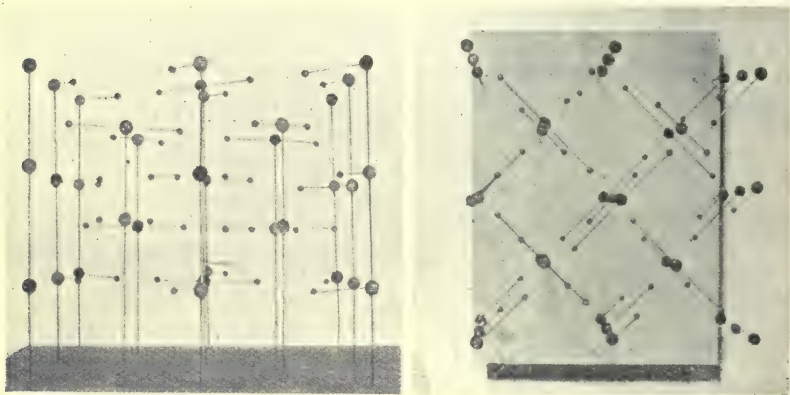


FIG. 568.—Model of the Zircon Structure.

affinity between silicon and oxygen than between zirconium and oxygen. In rutile and cassiterite all the metallic atoms are equal as regards their relation to the oxygen atoms, so that they cannot be considered as titanium titanate and tin stannate. A reproduction of a photograph of a model of the zircon structure is given in Fig. 568.

Now it is interesting that the arrangement, as just hinted, gives distinct evidence of molecular structure, that is, of the persistence of the existence of molecules in the solid state. For each of the zirconium or silicon atoms is associated with two oxygen atoms, the groups  $\text{SiO}_2$  and  $\text{ZrO}_2$  thus forming what may be described as "molecular elements" of the lattice, and there is evidence that the two groups  $\text{SiO}_2$  and  $\text{ZrO}_2$  are chemically saturated combinations. In support of this there is first the fact that the oxygen atoms are nearer to the silicon than to the zirconium atoms, and secondly another peculiarity of the lattice which renders the assumption of molecules a necessity. Fig. 569 will show this, for it will be clear from this figure that the triangle  $abc$  has a zirconium atom in two of its corners, and a silicon atom in the third. Now an oxygen

atom  $d$  will be equidistant from the zirconium atom  $b$  and the silicon atom  $c$ ; but the chemical affinity for Zr-O is different from that for Si-O, and if the position were dependent on these affinities then  $d$  could not be equidistant from  $b$  and  $c$ . The atom  $d$ , therefore, is attached chemically to  $a$ , as one of the two oxygen atoms held on either side of it, as shown in Fig. 569 joined by the straight line.

The lattice common to the zircon group has thus a molecular structure, with molecules of the type  $\text{MO}_2$ , where  $M$  may be silicon, zirconium, titanium, or tin. The three atoms forming one molecule are situated on a straight line, and with  $M$  in a central position. This line Vegard calls the molecular axis. He has determined the directions of the molecular axes and the distance to the central atom, thus fixing the positions of the oxygen atoms. The fact that the molecular distance is different for different central atoms is a strong argument in support of his view. The molecular axes are equally arranged and always perpendicular to the tetragonal axis, which accounts for the fact that the ratio  $c : a$  is smaller than unity and almost equal for all the minerals.

A curious and interesting result was afforded by thorite. This mineral is always found in what is known as the "metamict" form; that is, it shows the outer form of a crystal similar to zircon, yet an inner character which is isotropic. The lattice structure has broken down in the course of time and become vitreous. It was found to be incapable of reflecting any X-rays at all, although several very fine crystals were tested by Vegard.

In a later paper Vegard<sup>1</sup> gives the results of a study of xenotime  $\text{YPO}_4$ , and finds that it resembles zircon very closely. He then discusses the question, Is xenotime  $\text{YO}_2 \cdot \text{PO}_2$  like zircon  $\text{ZrO}_2 \cdot \text{SiO}_2$ , or is it really a phosphate of yttrium  $\text{YPO}_4$ ? He considers the latter the only possible view, having regard to the chemical nature of the substance. Consequently he somewhat modifies his strong remarks about the clear existence of molecules of  $\text{ZrO}_2$  and  $\text{SiO}_2$  in zircon. This modification to a view intermediate between his earlier view and that of von Groth, that no molecules exist in the solid state (which is certainly going too far), is probably an advance towards the real truth. He finally concludes as regards the zircon group, that they have a crystalline structure corresponding to  $\text{M}^1\text{O}_2 \cdot \text{M}^2\text{O}_2$ , which he calls the "constitution state" of the solid. But he considers further that this constitutional formula may be quite different from the chemical constitutional formula of the substances, or from the constitution of the liquid, gaseous, or ionic form.

Arrangement of atoms in  
(110) plane

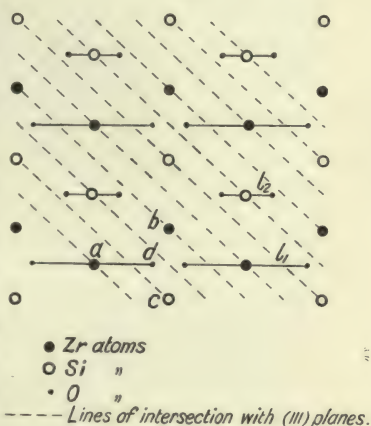


FIG. 569.—The Structure of Zircon.

<sup>1</sup> *Phil. Mag.*, 1917, 33, 421.



The chemical constitution of xenotime may be that of a phosphate, and that of zircon that of a silicate, yet identity of crystal structure does not necessarily involve identity or similarity of chemical constitution. This is due to the occurrence of more or less equalisation of the interatomic forces, which accompanies the close (maximum) proximity between the atoms of adjacent molecules which occurs in the solid state.

Williams<sup>1</sup> has also carried out an X-ray analysis of rutile and cassiterite, and proposes a different type of tetragonal structure as better suiting his observations of glancing angles and reflection intensities of the various X-ray spectra. The fundamental cell of rutile has the ratio  $c : a = 0.644$  and contains two molecules. It is made up of eight interpenetrating space-lattices, each having the translation ratio  $c : a = 0.644$ . From the abnormal intensities of the second order reflections from the (001) planes of atoms the oxygen atoms appear to be intercalated in these structural planes. The structure exhibits tetragonal screw axes, but is of holohedral symmetry.

Vegard<sup>2</sup> has also investigated **Anatase**, the other tetragonal form of  $\text{TiO}_2$  (see Chapter XIV.). He finds it to be such as is shown in the reproduction of photographs of models in Fig. 570. It is of the diamond type, but elongated along a four-fold axis to the extent corresponding to  $c : a = 1.765$ . It may be considered to be derived from zircon by removing the zirconium atoms and the associated pairs of oxygen atoms, and then substituting titanium atoms for the silicon atoms. The oxygen atoms can then no longer remain on horizontal molecular axes, but become arranged on vertical axes, parallel to the vertical axis  $c$ , as shown in the Figure. Each titanium atom has two oxygen atoms, one above it and one below, at distances equal to one-fifth of the vertical distance between successive titanium atoms. The deformation from a cube is then due to these vertically arranged oxygen atoms, which require for their insertion the extension of the tetragonal axis, and the ratio  $c : a$  thus becomes greater than unity.

**Copper Pyrites.**—Chalcopyrite,  $\text{CuFeS}_2$ , crystallises in the scalenohedral class 14 of the tetragonal system, with an axial ratio  $a : c = 1 : 0.9856$  (see page 200 with Fig. 160). Its structure has been investigated by C. L. Burdick and J. H. Ellis,<sup>3</sup> who find that the copper and iron atoms together form a face-centred cubic (really tetragonal) lattice (really point-system, there being no face-centred tetragonal space-lattice), the sulphur atoms occupying the centres of half the smaller cubes (more accurately rectangular blocks), selected tetrahedrally. It resembles zinc blende in which half of the Zn atoms are replaced by Cu atoms and the other half by Fe atoms. This work would appear to be capable of benefiting by revision, with greater accuracy, in view of Sir William Bragg's and Ewald's results with iron pyrites and hauerite.

**Orthorhombic Crystals—Sulphur.**—The common orthorhombic form of sulphur has been investigated by Sir W. H. Bragg, with results somewhat similar to those for quartz. The angles of reflection of the X-rays are

<sup>1</sup> *Proc. Roy. Soc., A*, 1917, 93, 418.

<sup>2</sup> *Phil. Mag.*, 1916, 32, 513.

<sup>3</sup> *Journ. Amer. Chem. Soc.*, 1917, 39, 2518.

all what would be expected from a rhombic space-lattice of type No. 8 (page 586), except as regards the reflections from the basal plane (001). The lattice is represented in Fig. 571. At first sight it resembles the

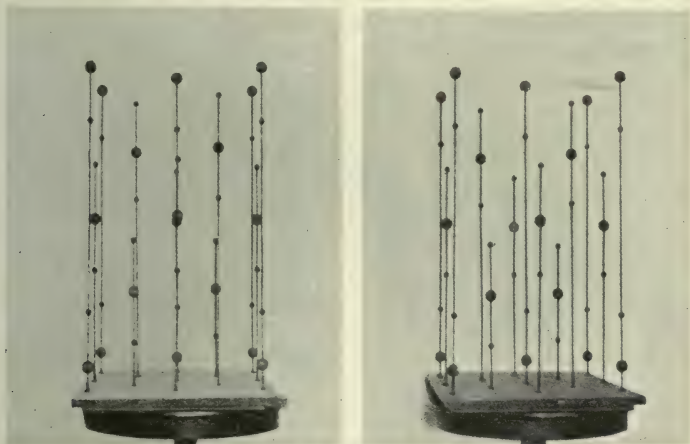


FIG. 570.—The Structure of Anatase.

orthorhombic rectangular space-lattice No. 10, in which the lengths of the three sets of edges are directly given by the axial ratios  $a:b:c=0.813:1:1.903$ . The form of cell suggested by Sir Wm. Bragg, however, will be observed to have a point at the centre of each basal plane. This makes it really into the space-lattice No. 8, of which the  $a$  and  $b$  axes are the diagonals. The fact that this is so is immediately recognised if one draws also an adjacent rectangular cell. A calculation of the number of sulphur atoms associated with each point of the space-lattice afforded the number 8, and subsequent calculation of the glancing angles of reflection agreed perfectly with the observed glancing angles, except for the basal plane, for which the observed angle was eight times the calculated value, corresponding to a spacing of one-eighth that of the lattice itself. Hence, there are eight interpenetrating space-lattices, just as there are three in quartz, evenly spaced along the vertical axis  $c$ . The sulphur atoms would appear, however, not to be all alike; there are at least two kinds indicated, four of each, and possibly even four kinds, in pairs. This remarkable and unusual occurrence may be connected with the well-known

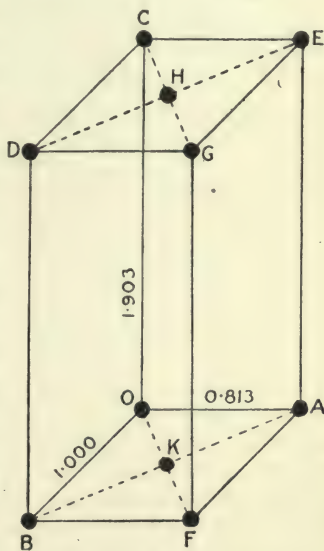


FIG. 571.—The Structure of Sulphur.

complexity of sulphur molecules (more than two atoms) in the vapourous condition near the boiling-point.

The case of sulphur is thus abnormal, and will require much further elucidation, like the case of quartz. A typical normal series of orthorhombic substances will be considered next.

**The Rhombic Alkali Sulphates.**—We now come to the consideration of the structure of the rhombic normal sulphates  $R_2SO_4$  where R is potassium, rubidium, caesium, and ammonium, the series of isomorphous salts which has been so fully worked out goniometrically and physically by the author, and the first member of which, potassium sulphate  $K_2SO_4$ , was taken in Chapter IV. as a typical crystalline substance for goniometrical measurement. The author suggested to Sir William Bragg that the X-ray analysis of this series of salts would be bound to give important information, and in particular would crucially test on the one hand the accuracy of the author's relative measures of the volumes and dimensions of the elementary cells of the space-lattices (the molecular volumes and topic axial ratios), and on the other hand the validity or otherwise of the valency volume theory of Barlow and Pope, which the author had shown to be incompatible with his results as regards the almost perfect isostructure of the ammonium and rubidium salts. Sir Wm. Bragg concurred, and arranged for the investigation to be carried out in his laboratory by Prof. Ogg and Mr. F. Lloyd Hopwood,<sup>1</sup> with crystals supplied by the author. It is very satisfactory that the results have indeed fully substantiated the author's measurements, derived from the goniometry and the density determinations, and have carried them to their logical conclusion, only possible since the discovery of the X-ray spectrometric method, by converting the author's relative measures into absolute volumes and lengths in space.

In the author's first paper in 1894 on these salts<sup>2</sup> it was pointed out that there was considerable evidence that the crystal unit, the smallest edifice possessing the complete details of symmetry of the crystal structure and which (considered as a point) by its regular repetition affords the space-lattice, was composed of four molecules of  $R_2SO_4$ . Now it is exceedingly interesting that Prof. Ogg and Mr. Hopwood find this to be a fact, indubitably indicated by their X-ray analysis. The rectangular parallel-pipedal cell, the edges of which are the  $a$ ,  $b$ ,  $c$  of their measurements, is that formed by taking analogously situated atoms, whether these be metallic, sulphur, or oxygen atoms, one from each set of four molecules to act as their representative point. In the author's later papers the idea of the necessity for identifying molecules at all in the crystal structure was not referred to, as the purely geometrical theory of crystal structure, now complete, regards the structure as essentially one of atoms. But the author has always considered this to be carrying geometry too far, further than either the chemistry or the physics of the organised solid, the crystal, warrants. For although the persistence of molecules in the solid state is not required by the geometrical theory of homogeneous structures, there are many reasons (which will be reverted to later in this chapter) for concluding that they do so persist, and no proofs whatever that they

<sup>1</sup> *Phil. Mag.*, 1916, 32, 518.

<sup>2</sup> *Journ. Chem. Soc.*, 1894, 65, 662.



do not. It is a satisfaction, therefore, to find that the work of Sir Wm. Bragg and his colleagues now shows that there is a real advantage in and necessity for thus marking off the molecules, if only in order to obtain a correct idea of the structure which is essential to the crystal as such.

The investigation is not yet complete as regards the details of the structure, but sufficient evidence has been obtained to show that the sulphur atoms are situated at the corners and centres of the faces of the unit cell, as shown in Fig. 572. Owing to the angles at the centre of the face of the rectangular rhomb bounded by  $a$  and  $b$  edges being near  $60^\circ$ , it is to be remarked that the sulphur atoms would thus exhibit a pseudo-hexagonal structure in planes parallel to the basal plane, the face (001). It was also indicated as probable that the metallic atoms are also arranged in hexagons. This is particularly interesting, for Fedorov has proposed (see p. 726) a pseudo-hexagonal structure for these rhombic sulphates, as being indicated by his crystallo-chemical analytical method of finding the correct setting of crystals. In deference to this, the author<sup>1</sup> recalculated the topic axial ratios for such a pseudo-hexagonal space-lattice, using the new densities which had just been determined. These ratios will be found in the table given on page 641. The points of the lattice were the same as for the rectangular lattice, but the diagonal distances between them were taken as forming four sides of the hexagon (two equal pairs), along with one of the rectangular axial directions only, which furnished the other two sides (one equal pair, but not quite equal to the others), such a lattice having angles of nearly exactly  $60^\circ$ . These facts are doubtless not unconnected with the remarkable manner in which the crystals often display a hexagonal appearance, sometimes by twinning (as in the well-known triplets of potassium sulphate shown on pages 512 and 513 in Figs. 418, 419, and 420, which resemble short hexagonal prisms doubly capped by pyramids), and sometimes by mere habit on the part of the single crystals (as in the case of the apparently hexagonal double pyramid of rubidium sulphate shown in Fig. 417 on page 512), the angles in the primary prism zone, formed by the faces of  $p$  {110} and  $b$  {010}, being very nearly  $30^\circ$  (only  $12'$  or  $13'$  from  $30^\circ 0'$ ). These pseudo-hexagonal topic axial ratios do not enable a comparison to be made with the measurements of Prof. Ogg and Mr. Hopwood, hence the author<sup>2</sup> published in the year 1917 the set of new values corresponding to the rectangular form which are given in the next table, on page 703, which will be shown to be remarkably concordant with those measurements. These rectangular topic axial ratios are similar to those given in the author's first (1894) paper on these salts, but are much more accurate,

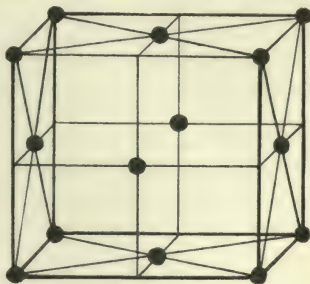


FIG. 572.—Sulphur Atoms in the Unit Cell of Alkali Sulphates.

<sup>1</sup> *Journ. Chem. Soc.*, 1905, 87, 1188.

<sup>2</sup> *Proc. Roy. Soc., A*, 1917, 93, 72.

owing to the newly determined and far more accurate densities having been employed in their calculation.

The mode of arriving at the results of Prof. Ogg and Mr. Hopwood may be briefly described. The actual distances between the centres of the sulphur<sup>1</sup> atoms forming the corners of the rectangular elementary cell, or, in other words, the distances between the consecutive planes in each of the three sets of parallel planes of atoms corresponding to the faces of the three primary pinakoids (100), (010), and (001), were obtained from the measurements of the glancing angles of reflection of the X-rays from these faces (in reality from the interior planes of atoms parallel to the faces). We have only to insert in the Bragg equation  $n\lambda = 2d \sin \theta$  (where  $n$  is the order of spectrum,  $\lambda$  is the wave-length of the X-radiation from the palladium anticathode used,  $\theta$  is the glancing angle of reflection of the X-rays, and  $d$  is the distance in question between successive planes of atoms) the observed value of the angle  $\theta$ , the wave-length  $\lambda$  (already determined by the use of the crystals best worked out by Sir Wm. Bragg, such as the alkali chlorides, and confirmed by independent methods) of the particular line of the spectrum of the radiation used, and the numerical order of the spectrum, in order at once to obtain the distance  $d$  required. For instance, when the value of  $\lambda$  for the line employed in the spectrum from the palladium anticathode used was  $0.584 \times 10^{-8}$ , and the glancing angle for this radiation in the second order spectrum reflected from the (100) face of potassium sulphate was  $5^\circ 51'$ , the value of  $d$  for planes of atoms parallel to this face was found to be :

$$d_{(100)} = 5.73 \times 10^{-8} \text{ cm.}$$

That this corresponds to a structural unit composed of four molecules is proved by the following :

Molecular weight of  $\text{K}_2\text{SO}_4 = 173.04$  ; density 2.666.

Ratio of crystal axes  $a : b : c = 0.5727 : 1 : 0.7418$ .

Mass of the hydrogen atom  $= 1.64 \times 10^{-24}$  gm.

Mass of unit rectangular rhomb of 4 molecules  $\text{K}_2\text{SO}_4$

$$= 4 \times 173.04 \times 1.64 \times 10^{-24} = 1135.1 \times 10^{-24} \text{ grm.,}$$

also  $abc \times 2.666 = 1135.1 \times 10^{-24} \text{ grm.}$

Then from the known axial ratio values of  $a : b : c$  we find

$$a = 5.731 \times 10^{-8} \text{ cm.,}$$

$$b = 10.008 \times 10^{-8} \text{ cm.,}$$

$$c = 7.424 \times 10^{-8} \text{ cm.}$$

$$\text{Volume of unit rhomb} = abc = 425.78 \times 10^{-24} \text{ c.c.}$$

The equality of the value of  $a$  and that for  $d_{(100)}$  obtained above shows that the assumption that there are four molecules of  $\text{K}_2\text{SO}_4$  in the elementary cell is correct.

<sup>1</sup> The metallic or oxygen atoms may here be equally as well specified as the sulphur atoms, provided they are similarly analogously chosen, one from each set of four molecules ; for the same space-lattice applies in common, being formed by any representative analogous points, one from every structural unit composed of four molecules.

Accepting then a unit cell composed of four molecules, that is, that four molecules are associated with each point of the orthorhombic space-lattice, the X-ray spectrometric observations lead to the spacings corresponding to the actual dimensions and volume of the cell which are given in the second of the two following tables, in the case of each of the four salts. A long list of the glancing angles observed is given in the memoir, and the agreement between them and the angles calculated on the assumption just stated affords ample confirmation of its truth.

MOLECULAR VOLUMES AND TOPIC AXIAL RATIOS (TUTTON).

Salt.	Molecular Volume.	Direct Results of Formulæ.	$\psi$ for $K_2SO_4=1$ .
		$\chi : \psi : \omega$ .	$\chi : \psi : \omega$ .
$K_2SO_4$ . .	64.91	3.0617 : 5.3460 : 3.9657	0.5727 : 1.0000 : 0.7418
$Rb_2SO_4$ . .	73.34	3.1778 : 5.5528 : 4.1562	0.5944 : 1.0387 : 0.7774
$(NH_4)_2SO_4$ . .	74.04	3.1788 : 5.6413 : 4.1289	0.5946 : 1.0552 : 0.7723
$Cs_2SO_4$ . .	84.58	3.3215 : 5.8149 : 4.3792	0.6213 : 1.0877 : 0.8191

ABSOLUTE DIMENSIONS OF SPACE-LATTICE CELL (OGG AND HOPWOOD).

Salt.	Length of Sides of Unit Rhomb.			Volume of Unit Rhomb.
	$a$	$b$	$c$	
	cm.	cm.	cm.	c.c.
$K_2SO_4$ . .	$5.731 \times 10^{-8}$	$10.008 \times 10^{-8}$	$7.424 \times 10^{-8}$	$425.78 \times 10^{-24}$
$Rb_2SO_4$ . .	$5.949 \times 10^{-8}$	$10.394 \times 10^{-8}$	$7.780 \times 10^{-8}$	$481.14 \times 10^{-24}$
$(NH_4)_2SO_4$ . .	$5.951 \times 10^{-8}$	$10.560 \times 10^{-8}$	$7.729 \times 10^{-8}$	$485.71 \times 10^{-24}$
$Cs_2SO_4$ . .	$6.218 \times 10^{-8}$	$10.884 \times 10^{-8}$	$8.198 \times 10^{-8}$	$554.88 \times 10^{-24}$

It is particularly interesting to compare these actual dimensions in space (given in the second table) of the unit cells of the four salts with the author's topic axial ratios and molecular volumes, which are quoted in the first of the two tables. These topic axial ratios are, as just mentioned, for the orthorhombic rectangular space-lattice, and were calculated with the aid of the author's most recently determined densities, obtained with the aid of the Retgers immersion method; these densities are given on page 641, together with the crystallographic axial ratios, and the topic axial ratios calculated on the pseudo-hexagonal scheme. The first series of topic axial ratios for the rectangular lattice, given in the first table above, were obtained by direct use of the formulæ:

$$\chi = \sqrt[3]{\frac{a^2V}{c}}, \quad \psi = \sqrt[3]{\frac{V}{ac}}, \quad \omega = \sqrt[3]{\frac{c^2V}{a}},$$

where  $a$ ,  $b$ ,  $c$  are the crystallographic axial ratios and  $V$  is the molecular volume. The second series in the first table, which are those to be directly compared with the absolute measurements of Ogg and Hopwood, are a simplified series obtained by dividing out the first series by the value



of  $\psi$  for the first salt of the series, potassium sulphate; the topic axial ratios being relative values, it is best to present them in their simplest form.

The actual lengths of the elementary cell edges given by Ogg and Hopwood are expressed in terms of  $10^{-8}$  cm., and the significant figures are just ten times greater than those of the relative distances given by the topic axial ratios. Hence, if " $10^{-7}$ " be written after each of the author's topic axial ratios (the series in which  $\psi$  for  $K_2SO_4=1$ ), these latter values become the actual distances in space. The degree of agreement is perhaps expressed too favourably by the tables, but the actual degree, as shown, for instance, by the result of the calculation for  $d_{(100)}$  (the length  $a$ ) for  $K_2SO_4$  already given, which was  $5.73 \times 10^{-8}$  cm., is sufficiently wonderful, being within 1 in 573. The total volumes given in the last column of Ogg and Hopwood's table show also precisely the same relations as the molecular volumes given in the second column of the first table.

The congruency or close approximation to identity of the structures of rubidium and ammonium sulphates, indicated by the molecular volumes and topic axial ratios published by the author (not only for these simple sulphates, but for every pair of the monoclinic double sulphates and selenates in which the R bases are rubidium and ammonium), is thus confirmed by absolute measurement by the X-ray spectrometric method. The absolute volumes of the unit cells of the space-lattices of the two salts are within 1 per cent of identity, just as are the molecular volumes, and the absolute lengths of the three edges for the two salts are correspondingly close to each other, and in a manner precisely like that shown by the topic axial ratios. It is thus fully substantiated that the constants molecular volume and topic axial ratios afford true indications of the relative volume and dimensions of the elementary space-lattice cells, in the cases of the crystal structures of isomorphous series. The correctness of the conception of topic axes was indeed proved by Sir W. H. Bragg for the isomorphous chloride and bromide of potassium, KCl and KBr, when he showed that the reflection angles bear the simple relationship demanded by their molecular volumes.

Now the volume of the unit cell of ammonium sulphate should be twice that of rubidium sulphate according to the valency volume theory of Barlow and Pope, if we assume triadic valency for nitrogen, since the sums of the fundamental valencies of  $(NH_4)_2SO_4$  and  $Rb_2SO_4$  are then respectively 24 and 12, and more than twice if nitrogen be pentadic (the volumes then being 28 to 12). The volumes of the unit cells of the two salts are now proved by direct X-ray measurement, however, to be nearly identical. Hence it is obvious that the valency volume theory does not represent a law of nature. The new method of analysis by X-rays has thus afforded a crucial test of the theory of Barlow and Pope, and the decision is against the theory.

**General Conclusions concerning X-ray Analysis of Crystals.**—The examples now given will have rendered it perfectly clear that in the opening up of this new domain of scientific investigation a very great advance

has been made. The structure of crystals has been carried beyond the realm of theory, based on external morphological and internal physical properties, and into the domain of assured fact. It must be regarded as eminently satisfactory that the new mode of attack by X-rays has resulted in the confirmation of all the principles which have been laid down in this book, and that in particular it has emphasised (1) the character of crystals as homogeneous structures, (2) the fundamental nature of the molecular or polymolecular space-lattice as the basis of that structure, (3) that the internal stereometry of (atomic distribution within) the space-lattice cell occurs strictly in accordance with one or other of the geometrically established systems of points, and (4) the value of the fruitful conceptions of molecular volume and topic axial ratios. Direct experimental proof is afforded that the structural units, the component chemical atoms and their molecular or polymolecular groups, are arranged in crystals in one or other of the 14 space-lattices as regards the main grosser structure (that of points representative of the molecule or small group of molecules), and in one or other of the 230 point-systems as regards the ultimate units, the chemical atoms themselves. This happy result indicates indubitably that crystallographers have recently been working on right lines, and that the arduous labour bestowed on the study and fine measurement, both of external angles and internal physical properties, of such small objects as the most perfectly formed crystals usually are, has not been in vain but has been fully rewarded by the absolute proofs now afforded by the X-ray analysis of the essential accuracy and intrinsic value of such painstaking work.

It is satisfactory that not only does X-ray analysis by the X-ray spectrometric method reveal the Bravais space-lattice, but also the more complicated point-system of Sohncke, Fedorov, and Schönflies. For more than half of the structures already elucidated have been shown to consist of several interpenetrating space-lattices, that is, of point-systems. Indeed, it must happen that the structure revealed by X-rays shall agree with one of the 230 types of homogeneous structures which alone are possible to crystals.

This new sphere of research, initiated by Laue with his radiograms and supplemented by the even more richly fertile spectrometric method of the Braggs, and the still more remarkable method of Debye and Scherrer, is now being explored by many other workers, and the number and type of crystalline substances thereby unravelled as regards their structure have lately been increased with considerable rapidity. The list has been notably extended by F. M. Jaeger, by Vegard, and by Rinne.<sup>1</sup> Jaeger,<sup>2</sup> in collaboration with H. Haga, has radiographed the following substances not mentioned in the preceding descriptions given in this chapter :

Cubic : sodium chlorate  $\text{NaClO}_3$  (see p. 1108), ammonium iron and potassium chrome alums  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

Tetragonal : d. and l. triethylenediaminecobaltic bromide.

Hexagonal-Trigonal : beryl  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , apatite  $\text{Ca}_5(\text{FCl})(\text{PO}_4)_3$ , ethyl

<sup>1</sup> *Ber. Kön. Sächs. Ges. Wiss. (Math.-Phys. Klasse)*, 1915, 67, 303

<sup>2</sup> *Proc. Kon. Akad. v. Wet.*, Amsterdam, 1914, 17. 438; 1915, 18, 1355 and 1552.

SPOT-PATTERNS FROM LAUE RADIOGRAMS OF HEXAGONAL AND TRIGONAL CRYSTALS, BY F. M. JAEGER.

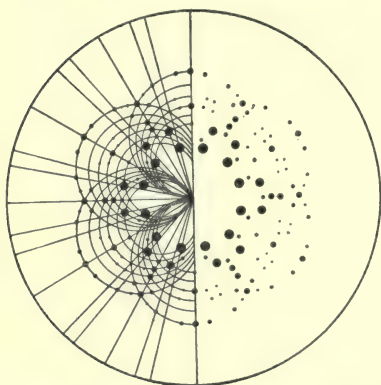


FIG. 573.—Beryl, plate parallel Basal Plane (0001).

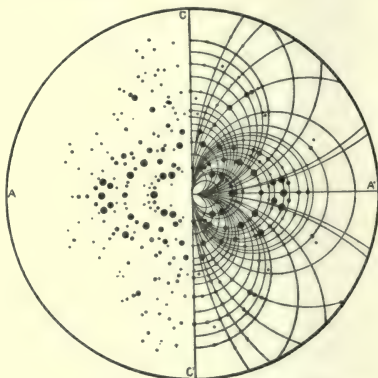


FIG. 574.—Beryl, plate parallel Hexagonal Prism Face (1010).

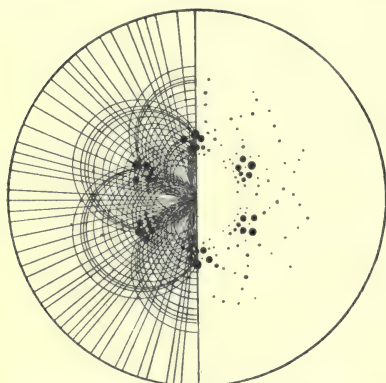


FIG. 575.—Apatite, plate parallel Basal Plane (0001).

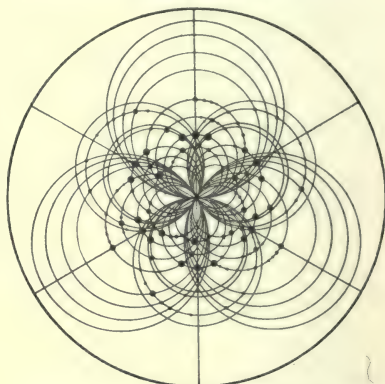


FIG. 576.—Phenacite, plate parallel Basal Plane (111).

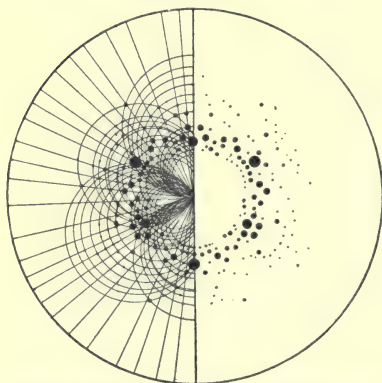


FIG. 577.—Tourmaline, plate parallel Basal Plane (111).

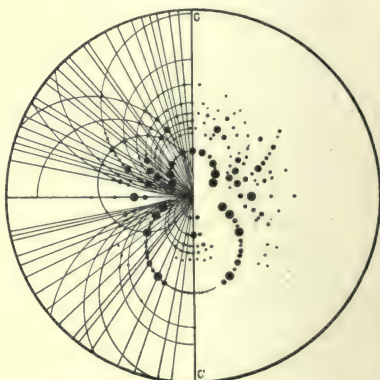


FIG. 578.—Tourmaline, plate parallel Hexagonal Prism Face (211).



SPOT-PATTERNS FROM LAUE RADIOGRAMS OF RHOMBIC CRYSTALS,  
BY F. M. JAEGER.

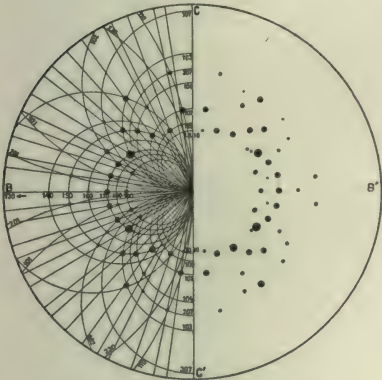


Fig. 579.—Aragonite parallel (100).

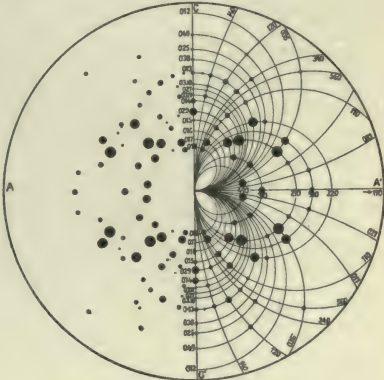


Fig. 580.—Topaz parallel (010).

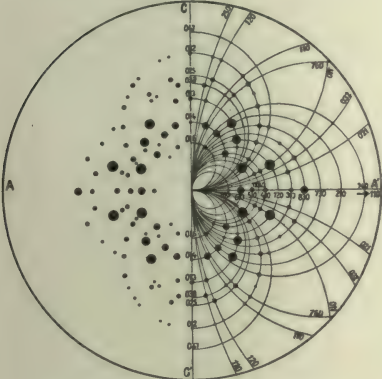


Fig. 581.—Hambergite parallel (010).

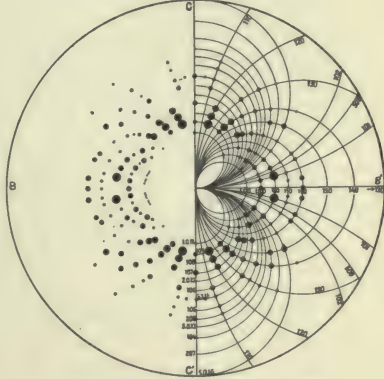


Fig. 582.—Struvite parallel (100).

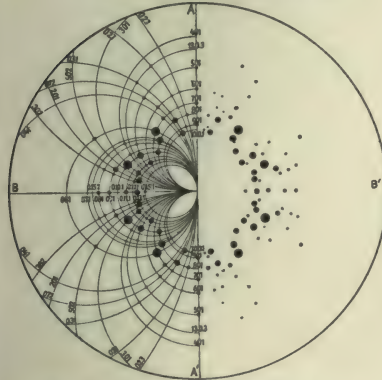


Fig. 583.—Hemimorphite parallel (001).

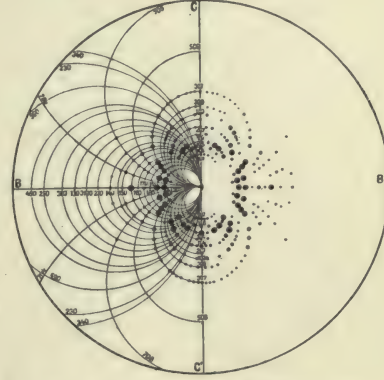


Fig. 584.—Zinc Sulphate parallel (100).

sulphates of rare earths  $R_2'''(SO_4 \cdot C_2H_5)_6 \cdot 18H_2O$ , in which R is any one of the 12 rare-earth metals, nepheline  $K_2Na_6Al_3Si_9O_{34}$ , dolomite  $CaMg(CO_3)_2$ , phenacite  $Be_2SiO_4$ , tourmaline  $H_6Na_2Fe_4B_6Al_3Si_{12}O_{63}$ , and cinnabar  $HgS$ .

Rhombic: aragonite  $CaCO_3$ , topaz  $(AlF)_2SiO_4$ , anhydrite  $CaSO_4$ , cordierite  $(MgFe)_4Al_4Si_5O_{18}$ , hambergite  $Be(OH)BO_3$ , hemimorphite  $H_2Zn_2SiO_5 = Zn_2(OH)_2SiO_3$ , struvite  $NH_4MgPO_4 \cdot 6H_2O$ , sodium ammonium d. tartrate  $C_4H_4O_6 \cdot Na \cdot NH_4$ , l. asparagine  $C_4H_8O_3N_2 \cdot H_2O$ , zinc sulphate,  $ZnSO_4 \cdot 7H_2O$ .

Rinne has published a magnificent series of Laue radiographic exposures of cuprite and rock salt (cubic), beryl (hexagonal), quartz, calcite, dolomite and carborundum (trigonal), anhydrite and aragonite (rhombic), diopside,  $CaMg(SiO_3)_2$ , epidote  $Ca_2Fe_2(FeOH)(SiO_4)_3$  and sucrose (cane-sugar)  $C_{12}H_{22}O_{11}$  (monoclinic), and of cyanite  $Al_2SiO_5$  (triclinic). His aragonite exposure (basal) exhibits 424 spots, furnished by as many planes of atoms belonging to 112 different forms, many of which have never been found actually developed as faces. He has also more recently<sup>1</sup> investigated the much discussed benitoite,  $BaTiSi_3O_9$ , and found it to be decidedly ditrigonal equatorial, class 22, as originally stated by Louderback. He recommends a Lilienfeld X-ray tube as giving the steadiest stream of rays of any desired "hardness." He states that great care is essential in adjusting the crystal, as otherwise want of symmetry is shown, and many of the so-called anomalies in Jaeger's radiograms are due to this cause.

Twelve of the best figures of Jaeger, unaffected by any abnormality due to insufficiently accurate adjustment, illustrating ten of the cases of trigonal, hexagonal, and rhombic symmetry studied by him and which have not been hitherto given in this chapter, are reproduced in Figs. 573 to 584, from separate copies kindly sent to the author by Prof. Jaeger.

Fig. 573 is the Röntgen pattern of spots afforded by a plate of hexagonal beryl parallel to the basal plane (0001). It shows a hexagonal axis and six vertical planes of symmetry, thus proving that beryl is really dihexagonal, and that the arguments of Viola against this supposition are not valid. Fig. 574 represents the diffraction pattern yielded by a plate of beryl parallel to a face of the hexagonal prism (10 $\bar{1}0$ ).

Fig. 575 is the Röntgen figure for a plate of hexagonal apatite parallel to the basal plane (0001). Fig. 576 is the diffraction pattern for a similar plate of trigonal phenacite, that is, parallel to the basal plane (0001) = (111).

The diffraction patterns of tourmaline plates parallel to (0001) = (111) and (10 $\bar{1}0$ ) = (2 $\bar{1}\bar{1}$ ) are respectively reproduced in Figs. 577 and 578.

The next six are all rhombic substances. Fig. 579 represents the diffraction pattern of spots for a plate of aragonite parallel to (100). Fig. 580 gives that for a plate of topaz parallel (010). Fig. 581 is the pattern for hambergite parallel (010). Fig. 582 represents the pattern afforded by a plate of struvite parallel (100). Next comes the figure for a plate of hemimorphite parallel (001) in Fig. 583. And Fig. 584 represents the Röntgenogram afforded by a plate of zinc sulphate parallel

<sup>1</sup> *Centr. Min.*, 1919, 193.

to (100). The orientation of the plates has been chosen so as to show the types of patterns for plates parallel to all three axial planes.

Jaeger<sup>1</sup> gives a useful construction for thus drawing the stereographic projection from the Röntgen pattern of spots.

Sir William Bragg has recommended that two fundamental reference constants shall be adopted, as having now (1921) been determined by several different observers with great care (especially Siegbahn and Uhler), namely, the spacing of the cube planes of rock-salt and the rhombohedron planes of calcite, the values being: for NaCl,  $d_{(100)} = 2.8140 \times 10^{-8}$  cm., and for  $\text{CaCO}_3$ ,  $d_{(100)} = 3.0279 \times 10^{-8}$  cm.

**X-ray Analysis of Organic Compounds.**—In his Presidential Address to the Physical Society on 11th November, 1921, Sir Wm. H. Bragg announced the first results of X-ray analyses of some aromatic carbon compounds. Benzene,  $\text{C}_6\text{H}_6$ , itself is not readily dealt with, as its crystals melt at  $6^\circ \text{C}$ . But naphthalene,  $\text{C}_{10}\text{H}_8$ , composed of two benzene rings with two carbon atoms in common, and several of its derivatives, and also anthracene,  $\text{C}_{14}\text{H}_{10}$ , with three rings and two carbon pairs in common, have been successfully tackled, the crystals of naphthalene by the ordinary Bragg method and most of the others by the powder method of the footnote on page 721. The monoclinic space-lattice cells of naphthalene were found to contain two molecules of the hydrocarbon, and their absolute dimensions were determined. The corners and face-centres appear to be occupied each by the double benzene ring as an actual structure-entity, a structure like a figure 8 built as a whole into the crystal edifice. Similarly, the larger cell of anthracene has the corners and face-centres occupied by triple ring-structures. The hydrogen atoms find their natural places in the spaces left around these ring-structures. Moreover, in all the derivatives of naphthalene investigated, the double ring-structures appear to persist as such. Thus the very interesting and important fact stands out, that the benzene ring or its condensed multiple appears to remain intact and to enter the crystals of the aromatic compounds as an entity. It is also interesting to recall that the ring-structure of benzene corresponds to the graphitic form of carbon, as shown on page 692. Incidentally these striking results give very strong support to the view that molecules continue to persist in the crystalline state.

**The Bearing of X-ray Analysis of Crystals on the Existence of Molecules in the Solid Crystalline State.**—It has thus been sufficiently proved that the scattering of X-rays by reflection or diffraction at the planes of atoms in crystals is essentially a function of these atoms themselves, and is owing to the close approximation of the order of size of the atoms to that of the wave-length of the X-radiation. The fact, however, that so many of the substances studied by the Bragg method have been found to possess polymolecular elementary space-lattice cells (for instance, the four-molecule cells of the alkali sulphates) does not point to the non-persistence of molecules in the crystal, and the conclusion of von Groth, soon after the inception of the new method of research by X-rays, that chemical molecules do not exist in the crystalline condition, is therefore at least

<sup>1</sup> *Proc. Kon. Akad. v. Wet.*, Amsterdam, 1915, 18, 1552.



premature, and in the view of the author will prove in the end to be incorrect. It will be shown in Chapter LX. that the researches both of Lehmann and his critics, with regard to the so-called "liquid crystals," have combined in showing that the molecular forces are undoubtedly still very lively in the intermediate state between true liquid and true solid, that of the "liquid crystal." The intermolecular forces are, in fact, adequate to bring about a regular orientation of the molecules or polymolecular particles with respect to one molecular axis. Indeed the elongated molecules of these viscous substances become orientated with their principal axes parallel, thus giving rise to the swarm, which is an approximation to an optically uniaxial crystal. There can also be no question but that the growth of a crystal is to be attributed to the special properties of the surface of the solid crystal structure already laid down, whereby further accretions of growth occur. In all probability the exterior electrons, those of the outer shell (by some physicists considered as roving or valency electrons), are largely concerned. The whole process of the passage from liquid to crystal is so continuous, and the natural succession of phases—gas, liquid, liquid crystal, and true solid crystal—follow so unbrokenly, that to deny the continued existence of the molecule at any stage is illogical. The fact that the persistence of the molecule is not absolutely essential to the geometrical explanation of crystal structure is not a valid argument for denying that persistence. Moreover, Barker<sup>1</sup> has truly observed that to deny the existence of the chemical molecule in the solid crystalline state would open up most extensive possibilities of isomeric change, optical inversions, and so forth, whenever the crystalline structure is broken down by dissolving the solid in a solvent or by subjecting it to fusion. That such changes have never been observed is a strong argument in support of the persistence of the molecule throughout. The persistence of the molecule in the cases of complicated molecules composed of many atoms must, indeed, be perfectly obvious, and very direct evidence is afforded by the naphthalene and anthracene compounds. The close approximation of the molecules in the act of crystallisation may yet occur without destruction of the interatomic forces which retain the molecules as such. There may be a certain amount of pooling of the chemical affinities when the atoms are brought into such close neighbourhood that those belonging to different molecules are little if any further removed from each other than those of any one and the same molecule; indeed, it is likely that these forces exerted at close quarters by the atoms of one molecule on those of other approaching molecules together constitute the directive force of crystallisation, which determines the type of crystalline structure produced. In any case, at the first opportunity, such as that afforded by solution or fusion for instance, the same molecules or others indistinguishable from them are again restored as freely moving separate entities. Also only concentrated, indeed supersaturated, and not dilute solutions are concerned in crystallisation, so that electrolytic dissociation and ionisation are excluded.

Besides the strong evidence referred to on the preceding page some very

<sup>1</sup> *Chem. Soc. Annual Report*, 1914, 247.

definite evidence has been advanced by A. Smits and F. E. C. Scheffer,<sup>1</sup> by A. Reis,<sup>2</sup> by Stark and by Beckenkamp, of the existence of molecules in the solid crystal. Especially do Stark's experiments on electro-affinity render it impossible that intra-molecular linkings are destroyed in the crystalline state. Also the behaviour of crystals towards infra-red radiation, studied by Reis, has clearly indicated molecular intactness in the solid state; for instance, all carbonates have been found to exhibit an intense reflection of infra-red rays of a specific wave-length, as well in the state of solid crystal as in a state of fusion or solution.

**Law of Atomic Diameters.**—A careful scrutiny of the remarkable analyses of crystal structure which have been effected by the use of X-rays, as described in the preceding pages, supplemented recently by some additional measurements with the X-ray spectrometer, has led to the revelation of a further fact which appears likely to prove of considerable assistance in tackling more complicated crystal structures, especially those of more complex crystallised chemical compounds. This new fact is that the atoms of each chemical element, in all the compounds containing it which have been studied, possess the same fixed and definite diameter (regarding the atom as a sphere), and that these constant atomic dimensions of the different elements are related, not as the valencies of the elements (as Pope and Barlow's theory stipulates), but in a manner which is very similar to the variation of their atomic volumes as exhibited in the well-known periodic curve of Lothar Meyer. Moreover, when the crystal is that of an element itself the distance between the centres of the atoms is actually equal to this diameter, that is, to two atomic radii, so that the spheres to which these dimensions refer are in contact. When it is a crystal of a chemical compound that is under investigation, the distance separating the centres of any two contiguous atoms in the structure is equal to the sum of their radii, whether the atoms be those of the same or of different elements. The closest observed positions of the two atoms are, of course, those for which these minimum distances of separation in question are measured, nearer than which they are never found to approach. Thus, in general, the actual distance of separation of the centres of any two such adjacent atoms in a crystal structure is found in absolute measure, as determined by the X-ray spectrometer, to be equal to the sum of two constants (assuming the more general case when the atoms are of two different elements), namely, the radius of the atom in each case. This radius, or its double, the atomic diameter, has been actually determined for a considerable number of elements, both from the pure solid crystallised element itself and from crystallised compounds of the element with other elements. The simplest manner of regarding this constant distance is to imagine it as the radius of a sphere; whether the sphere be the outer electronic shell of the atom itself, or the sphere of influence of the atom, is immaterial, so long as it is understood to be that sphere within which no other atom can penetrate, and which acts as the contact sphere towards the spheres of neighbouring atoms. It is best termed the

<sup>1</sup> *Proc. Kon. Akad. Wetensch.*, Amsterdam, 1916, 19, 432.

<sup>2</sup> *Zeitschr. für Elektrochemie*, 1920, 26, 408 and 412.

"Atomic Domain." It may quite well be the actual outer shell of the electrons of the atom, or it may correspond to the Beilby pulsation cell, or to the Pope and Barlow sphere of influence; in any case the essential fact is that the radius of this sphere of atomic domain is actually that given in absolute measure by the X-ray spectrometric measurements.

This further advance was first clearly established by Prof. W. L. Bragg, in an Evening Discourse at the Royal Institution on Friday, May 28, 1920, an account of which was published in the *Philosophical Magazine* for August 1920 (vol. 40, page 169), as well as by the Royal Institution shortly afterwards. A table of atomic diameters was given, and is quoted on page 713. It was also expressed graphically in a curve-diagram which is reproduced in Fig. 584*a*, by kind permission of Prof. Bragg. In this diagram atomic numbers of the elements are taken as abscissæ, and atomic diameters or radii as ordinates.<sup>1</sup> The strongly electro-

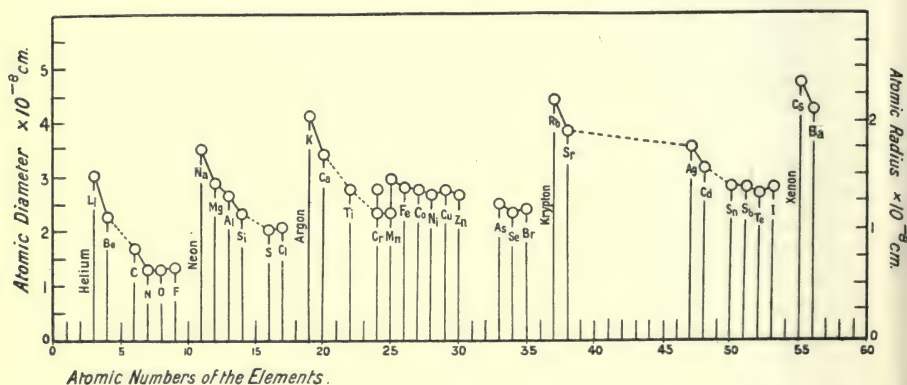


FIG. 584*a*.—Curve-diagram of Atomic Diameters in Ångström Units ( $10^{-8}$  cm.).

positive alkali metals head each period with the greatest atomic diameter, followed by the alkaline earths, and the diameter steadily diminishes as the atomic number or atomic weight increases, until it reaches a minimum for the electro-negative elements at the end of a period. From this curve it will be clear that valency has nothing to do with the atomic dimensions; for the atom of oxygen, for instance, of valency two, and nitrogen of valency three or five, possess the minimum diameter ( $1.30 \times 10^{-8}$ ), while lithium, sodium, potassium, rubidium, and caesium, of valency only one, possess atomic diameters ranging progressively with the atomic number from  $3.00 \times 10^{-8}$  cm. to  $4.75 \times 10^{-8}$  cm., that is, from twice to more than three and a half times the diameter of the oxygen or nitrogen atom. Indeed caesium, the most electro-positive element known, possesses the atoms of largest diameter. The atomic diameters are thus periodic functions of the atomic number or atomic weight. Atomic number is best referred to as having the definite relation to the structure of the

<sup>1</sup> To obtain the atomic diameter or radius from the curve multiply the reading of the ordinate scale given on the left or right by  $10^{-8}$  cm.



atom so clearly expressed by the law of Moseley (see page 744). The atomic diameter given for carbon is probably somewhat high, 1.35 Å being probably more accurate for carbon in compounds.

The table of atomic diameters is followed by another, in which ten examples, chosen typically from among the cases of crystal structure analysed in the preceding pages, are given of the operation of the new law, the sum of the radii of two adjacent atoms of different elements being compared with the distance of the atomic centres as actually measured by X-rays. The agreement is remarkably good, and the slight differences are about equally distributed on both sides of zero.

It has long been known that the molecular volume of a compound is not as a rule the sum of the atomic volumes of its component elements, a notable contraction usually occurring on the combination of the elements. This contraction is now seen to be due, not to differences in the sizes of the atoms or their spheres of influence, but to the difference in the crystal structure of the solid element and the solid compound. In examining carefully all the *data* put forward by Prof. Bragg there is a very satisfactory consensus of agreement, pointing at least to the approximate truth of the new law of atomic diameters, which is all that Prof. Bragg claims for it. It is bound, however, even if only approximate, to be of great help in interpreting the results of X-ray analysis. For no two atoms can have, or be assigned, closer positions than the sum of their atomic radii, and thus one of several alternative possibilities of structure must usually be clearly indicated as the only possible correct one.

#### ATOMIC DIAMETERS, IN ÅNGSTRÖM UNITS.

$$\text{Å} = 10^{-8} \text{ cm.}$$

Atomic Number.	Element.	Atomic Diameter.	Atomic Number.	Element.	Atomic Diameter.
3	Lithium . . .	3.00	26	Iron . . .	2.80
4	Beryllium . . .	2.30	27	Cobalt . . .	2.75
6	Carbon . . .	1.54	28	Nickel . . .	2.70
7	Nitrogen . . .	1.30	29	Copper . . .	2.75
8	Oxygen . . .	1.30	30	Zinc . . .	2.65
9	Fluorine . . .	1.35	33	Arsenic . . .	2.52
11	Sodium . . .	3.55	34	Selenium . . .	2.35
12	Magnesium . . .	2.85	35	Bromine . . .	2.38
13	Aluminium . . .	2.70	37	Rubidium . . .	4.50
14	Silicon . . .	2.35	38	Strontium . . .	3.90
16	Sulphur . . .	2.05	47	Silver . . .	3.55
17	Chlorine . . .	2.10	48	Cadmium . . .	3.20
19	Potassium . . .	4.15	50	Tin . . .	2.80
20	Calcium . . .	3.40	51	Antimony . . .	2.80
22	Titanium . . .	2.80	52	Tellurium . . .	2.65
24	Chromium . . .	2.80	53	Iodine . . .	2.80
	" { (electro- )	2.35	55	Cæsium . . .	4.75
	" { (negative) }		56	Barium . . .	4.20
25	Manganese . . .	2.95	81	Thallium . . .	4.50
	" { (electro- )	2.35	82	Lead . . .	3.80
	" { (negative) }		83	Bismuth . . .	2.96

## TEN EXAMPLES OF OPERATION OF LAW OF ATOMIC DIAMETERS.

Compound.	Atomic Centres.	Sums of Radii in Å.	Observed Distance in Å.	Difference in Å.
NaCl	Na, Cl	$1.77 + 1.05 = 2.82$	2.80	-0.02
KCl	K, Cl	$2.07 + 1.05 = 3.12$	3.13	+0.01
KBr	K, Br	$2.07 + 1.19 = 3.26$	3.28	+0.02
CaF <sub>2</sub>	Ca, F	$1.70 + 0.65 = 2.35$	2.34	-0.01
CaCO <sub>3</sub>	Ca, O	$1.70 + 0.65 = 2.35$	2.30	-0.05
MnCO <sub>3</sub>	Mn, O	$1.47 + 0.65 = 2.12$	2.10	-0.02
FeCO <sub>3</sub>	Fe, O	$1.40 + 0.65 = 2.05$	2.04	-0.01
Al <sub>2</sub> O <sub>3</sub>	Al, O	$1.35 + 0.65 = 2.00$	2.02	+0.02
ZnO	Zn, O	$1.32 + 0.65 = 1.97$	1.97	0.00
ZnS	Zn, S	$1.32 + 1.02 = 2.34$	2.35	+0.01

It will have been observed that there are two very distinct types of structure among the many dealt with in the preceding pages, namely, (1) those in which the positions of the whole of the atoms present in the compound are fixed in the crystal structure by the symmetry, that is, by the nature of the space-lattices or other point-systems according to which they are assembled; and (2) those in which, while the positions of the atoms of one or more of the elements (the metal, for instance) are thus fixed by the symmetry, the positions of other atoms (oxygen or sulphur, for instance) are permitted a certain amount of latitude by the symmetry, within the range of which it is the function of X-ray analysis to determine the precise spots where they are located. Sodium and potassium chlorides are examples of the first type, and iron pyrites, FeS<sub>2</sub>, and calcite, CaCO<sub>3</sub>, are instances of the second. For the positions of the sulphur and oxygen atoms in the two latter compounds are allowed a certain choice of position along particular lines (see Figs. 554, 555, and 560), the exact position being only determinable by quantitative X-ray spectrometric measurement; the iron and calcium atoms, however, are fixed in definite positions by the symmetry of the space-lattice, at the nodes of which they lie. In both these cases there is only one such "parameter" to be determined, but in ruby, Al<sub>2</sub>O<sub>3</sub>, two different parameters have actually to be measured by X-rays, and in quartz, SiO<sub>2</sub>, no less than four, before the positions of the oxygen atoms can be absolutely located. It is this necessity of measuring parameters (using the word in the sense meant by Prof. Bragg, the definition of the position of an atom along a line, usually an axis or a diagonal, and not in its ordinary crystallographic sense) which renders the elucidation of the crystal structure of the more complex substances so much more difficult than that of the simpler ones first dealt with by the X-ray method. As already frequently pointed out, it is often very difficult to arrive at the correct interpretation of the indications of the X-ray spectrometer, as regards especially the intensities of the different orders of X-ray spectra, so that any further principle assisting in the diagnosis is of the utmost value. It is already apparent that in the new knowledge concerning the atomic diameters we have just such a welcome aid as was so desirable. This knowledge, that the distances separating the centres

of the atoms from those of their nearest neighbours are in all cases the sums of the atomic radii, must now be used to test all further cases where difficulty is met with, and will probably result in the successful solution of many otherwise insoluble cases.

One case may perhaps be taken as an example, to render the principle quite clear, that of iron pyrites,  $\text{FeS}_2$ , which is a very instructive one. Fig. 584*b* shows at *a* one of the eight small cubes (the lower left front one) of the larger unit cube shown in the form of a model at *b* in the figure, resembling the upper left front one in Fig. 555. The sulphur atom  $S_1$  will have as its nearest neighbour the sulphur atom  $S_2$ , at a like distance from and beyond G, as each cube corner is a centre of symmetry. Hence,  $S_1G = S_2G$ , and  $S_1S_2$  will be the distance between the atomic centres, equal to the atomic diameter of sulphur 2.05 Å. There is no

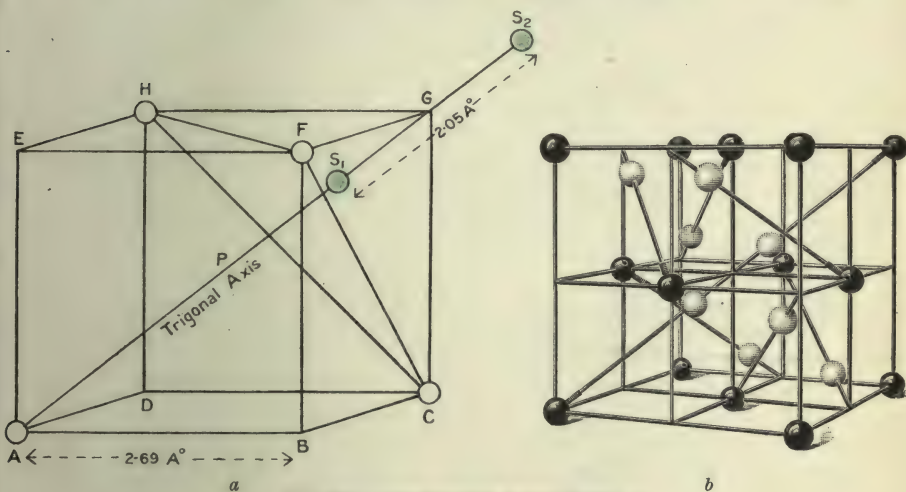


FIG. 584*b*.—The Structure of Iron Pyrites.

iron atom at this corner G, so the  $S_1$  atom of sulphur will be packed in between its neighbouring sulphur atom  $S_2$  and the three iron atoms at H, F, and C. Now the structure of metallic iron has been determined by Hull (see page 693) to be the cube-centred lattice, and from the measured distances of the planes of iron atoms the diameter of the iron atom has been obtained, after which it only requires a simple application of geometry to determine the distance of the centre of the sulphur atom from the corner G, remembering that it touches the three iron atoms and the other sulphur atom. In this manner it has been found that the distance separating the centres of the two sulphur atoms  $S_1S_2$ , and therefore the atomic diameter of sulphur, is 2.05 Å.

Prof. Bragg considers that the explanation of this additive law of atomic diameters is afforded by the version of the theory of atomic structure which has been put forward by G. N. Lewis<sup>1</sup> and I. Langmuir.<sup>2</sup>

<sup>1</sup> *Journ. Amer. Chem. Soc.*, 1916, 38, 762.

<sup>2</sup> *Ibid.*, 1919, 41, 868.



It differs from the Bohr version in considering the negative electrons surrounding the positively charged nucleus to occupy approximately fixed positions, more or less cubical in character, on spherical shells, and that the maximum possible stability is attained when the arrangement is that which obtains in the elements of the argon inert gas group. For helium this means 2 electrons in the outer shell, for neon and argon 8, for krypton and xenon 18, and for niton 32. The diameters of these outer shells of the inert gas, as derived indirectly, would appear to be: for neon  $1.30 \text{ \AA}$ , argon  $2.05 \text{ \AA}$ , krypton  $2.35 \text{ \AA}$ , and xenon  $2.70 \text{ \AA}$ . The chemical activity of the other elements is supposed to be due to their endeavour to attain this condition of stability of the outer shell of electrons. For instance, potassium—having the atomic number 19, and therefore a nucleus of positive charge 19 and 19 negative electrons to correspond—possesses one more electron than argon (atomic number, etc., 18), and endeavours to give it up in order to revert to the stabler outer shell condition of argon. On the other hand, chlorine, of atomic number, positive nuclear charge, and number of electrons all 17, is ready to take up an electron in order to attain the same object. Hence, the electro-positive potassium and the electro-negative chlorine combine with the greatest facility to produce a stable molecule, the atoms being held together by the mutual electrostatic attraction of the extra positive charge now possessed by the potassium atom (due to the loss of the hitherto compensating negative electron) and the extra negative electron (over and above that required to compensate for the positive charge on its nucleus) now possessed by the chlorine atom. In the solid crystal the greatest stability is attained when each atom of either element is surrounded by six atoms of the other, as shown in Fig. 540, and in the model represented at *a* in Fig. 584c. The attraction being equal towards each of the six, it is difficult, as already stated on page 709, to consider molecules as either existing or persisting as such in the crystalline state. Yet during the approach to the process of crystallisation from a supersaturated solution or the fused state, and the moment the crystalline structure is taken to pieces, say on solution by a solvent or by melting, the compound clearly possesses in the one case, and obviously resumes in the other case, the true molecular character.

The chemical combination of two electro-negative elements occurs in a different manner, namely, by holding pairs of electrons in common (a "pair" being usually one from each atom), both atoms individually having fewer electrons than correspond to the complete stable system as it obtains in the argon group. Carbon dioxide and sulphur dioxide are cases in point.

Calcite offers an example of both types of chemical combination. The calcium atom, represented by each large sphere in the model illustrated at *b* and *c* in Fig. 584c, is an ion with a double positive charge, while the  $\text{CO}_3$  group acts as an ion with a double negative charge. The two kinds of ions group themselves in calcite very similarly to those of potassium and chlorine in sylvine, but the greater complication of the  $\text{CO}_3$  group deforms the cube into a rhombohedron. The carbon and oxygen atoms of this

group, as they share electrons, are more closely knitted together, and are represented by the two kinds of smaller spheres in the model. This will be particularly evident at *c* in Fig. 584*c*, which shows the model taken to pieces to illustrate the arrangements of the atoms in the (111) planes. The size of the calcium atom is relatively exaggerated, but the oxygen and carbon atoms are in about correct proportion to each other, and at

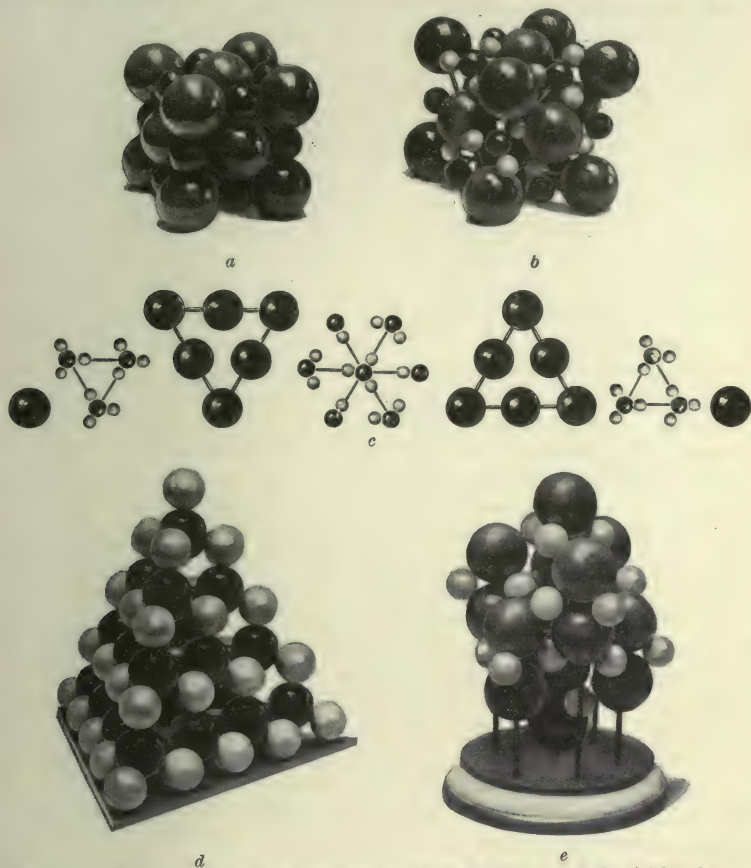


FIG. 584*c*.—Models representing the Structure of KCl or NaCl (at *a*),  $\text{CaCO}_3$  (at *b* and *c*), ZnS (at *d*), and  $\text{Al}_2\text{O}_3$  (at *e*).

about the correct distance from each other; as these atoms hold electrons in common, the distance between their atomic centres is approximately equal to the sum of their atomic radii. The electro-positive elements never share electrons, and are therefore isolated in the crystal structure and occupy a larger domain.

The models at *d* and *e* represent the structures of zinc blende and alumina (ruby or sapphire) respectively.

An instructive instance illustrating the dependence of the dimen-

sions on the amount of residuary charge (above or below the stable shell arrangement) is afforded by the crystals of sodium fluoride, NaF, and of magnesium oxide, MgO. Both are of similar cubic structure to rock-salt and sylvine, and the elements present tend to take up the same stable electronic condition obtaining in neon. But as the ions in magnesium oxide carry charges twice as great as those in sodium fluoride, the structural dimensions in magnesium oxide are much smaller, the side of the elementary cube being  $4.78 \times 10^{-8}$  cm. in sodium fluoride, but only  $4.22 \times 10^{-8}$  cm. in magnesium oxide.

Carbon and nitrogen, as well as oxygen, also tend to take up the neon form of stability, with eight electrons in the outer shell (and two in the inner one). Carbon has four electrons in its outer shell, and in order to take up this stable arrangement, when crystallised as the diamond, it shares an electron with each of the four neighbouring carbon atoms (it will be remembered that every carbon atom in the diamond is surrounded by four others symmetrically, at the corners of a regular tetrahedron). The great density and hardness of the diamond is thus accounted for.

It will be observed that when chromium and manganese are acting in their acid-forming capacity in the chromates and manganates, and are thus sharing electrons with other atoms, they possess the same atomic diameter as selenium. This is in perfect agreement with the isomorphism of these salts with the selenates and sulphates, and the very close approximation of their molecular volumes to those of the selenates.

The reason why the electro-negative elements exhibit the smallest atomic diameters in the periodic curve of Fig. 584a, or in the table given on page 713, will now, therefore, be perfectly clear, namely, because of this sharing of the electrons in their outer shells. The reason for the larger diameters of the electro-positive elements has also been made equally obvious, namely, because they do not share electrons in their outer shells, with neighbouring atoms, and are therefore situated at a further distance from other atoms, and so occupy a greater space in the crystal structure.

The meaning of the term "atomic diameter" may thus be taken to be "the diameter of the outer shell of electrons" as defined by Langmuir.

It is highly interesting that Prof. A. O. Rankine<sup>1</sup> has just shown that trustworthy comparative data for the sizes of the atoms of nine of the elements given in the table on page 713 are available from quite a different source, namely, for the four inert gases, the three halogen gases, oxygen, and nitrogen. The source in question is the measurement of viscosity, which has been very accurately carried out in a series of researches by Rankine for all these gases. From these determinations it has been possible to discover the nearest approach of the centres of two atoms during a collision, and the values thus obtained, in the cases of the inert gases, for the atomic diameters expressed in Ångström units, are: neon 2.35, argon 2.87, krypton 3.19, and xenon 3.51. They are, as was

<sup>1</sup> *Phil. Mag.*, 1920, 40, 518. The values given in this paper were: neon 2.02, argon 2.56, krypton 2.76, and xenon 3.06. More accurate results have since been obtained, and are those given above, which have been communicated direct to the author by Profs. Rankine and Bragg.



to be expected, very slightly greater than W. L. Bragg's atomic diameters ; for even when two atoms of these monatomic gases collide, there is a sort of cushion or film of resiliency or repulsion between them, preventing absolute contact of the outer shells, as otherwise they would become attached to each other. So the result is eminently satisfactory. The other five gases form diatomic molecules, so that a chlorine molecule is practically like two argon atoms in contact, a bromine molecule has the shape and size of two krypton atoms, and an iodine molecule is similarly related to two xenon atoms. Taking these facts into account, the viscosity experiments yield the atomic diameters : chlorine 2.54, bromine 2.71, and iodine 2.98. These are again slightly greater than the values derived from X-ray crystal analysis. The molecules of oxygen and nitrogen are of similar dimensions to two atoms of neon in contact, and afford viscosity results pointing to atomic diameters also just slightly greater than those obtained by W. L. Bragg from crystal X-ray measurements. Prof. W. L. Bragg, in a note to the author after the appearance of Rankine's memoir, supplies the following additional interesting information : "The figures given by the kinetic theory are naturally greater than the estimates of the size of the outer electron shells. In crystals, where the atoms do not hold electrons in common, one always finds a gap between the two outer electron shells of the neighbouring atoms. For instance, in the NaCl series of compounds, this gap is always about 1.10 Å, and for the CaO series of compounds 0.80 Å. It is rather interesting to note that two inert gas atoms, in collision, have about the same gap between their outer shells, when they are 'in contact,' as do the atoms in these salts. The most important point, however, is that the increase from neon to argon, argon to krypton, and krypton to xenon, is very nearly the same when deduced from the positions of the atoms in the crystals and from the viscosity of the inert gases." Thus the Law of Atomic Diameters is remarkably supported by these independent measurements by Rankine.

Further details of the Lewis-Langmuir theory will be found in Chapter XXXV. Its value and correctness can only be tested by further research, but it certainly appears to explain the new facts brought to light in these later X-ray investigations of crystals in a manner more satisfactory than the Bohr version of the atomic structure theory.

**Experiments to locate the Electrons of the Atom.**—If the electrons, especially those of the outer shell, are more or less fixed in position about the atom, it would appear probable that still more careful X-ray exploration should locate them. In this regard Sir William Bragg has most kindly made to the author the following very interesting communication, for inclusion in this chapter :

"I have been working at the existence or non-existence of the second order spectrum in the tetrahedron planes in the diamond. In our earlier work we found none within the limits of errors of observation of that date. Debye has since then hunted for it by the photographic method but has not found it. However, I have now obtained distinct evidence of its existence. The meaning of it is that alternate atom-bearing planes of carbon atoms in the diamond are not absolutely alike. For instance, if

the carbon atom had in itself a tetrahedron arrangement of electrons, the effect would be explained. It would also be explained by any other character of the atom which would distinguish it from being a perfect sphere with similar properties in every direction from the centre, this character being again disposed tetrahedrally. There might be connecting electrons or something equivalent thereto between the atoms. This again must be disposed tetrahedrally and would seem to imply something tetrahedral in the atom, for the electrons to fit on to. It is very curious that the effect is very small, which would seem to imply that such connecting electrons—if it be really they which are causing the existence of the spectrum in the second order—have very feeble action on the X-rays.

“We get results having the same kind of interpretation with fluorspar, on which Mr. Pealing has been working in my laboratory. The first order of the spectrum from the cube face is excessively minute. As has already been explained, the effect is that the calcium and the fluorine planes have very nearly equal action on the X-rays. But the curious thing is that the third order spectrum, which one would naturally expect to be smaller still, is really much bigger; the fourth is also much bigger than it should be. Of course, the even order spectra are, as a rule, far larger than the odd order spectra; indeed, the odd orders are not easy to find at all. The interpretations of these facts would be that there is some weak diffracting centre about one-third to one-quarter the way between calcium and fluorine planes, and these again might be connecting electrons or more generally singularities at the points of junction between the calcium and fluorine atoms.

“These results illustrate the fact that the X-ray methods may well be expected to give us information about the distribution of the electrons in or about the atom, and so far these indications point to the existence of stationary electrons, or at least of electrons having average positions which are not in the centre of the atom. This again fits in with the idea that the atoms in the crystal are not packed into the smallest possible volume, but form a sort of structure in which relatively large empty spaces are left. The atoms, so to speak, are not only guided by the effort to get as close as possible to each other; they try to attach themselves to one another at definite points on their surfaces.”

These very interesting results, so kindly communicated by Sir William Bragg and quoted above intact, would appear to foreshadow yet another departure of a still more fascinating character, going beyond the mere structure of the crystal to that of the atoms composing it, and especially as regards the disposition of the outer electrons, and the nature of the linkages or other relations between them. Their bearing on the Lewis-Langmuir version of the theory of atomic structure will be obvious. Moreover, the indication of relatively large empty spaces is a most welcome confirmation of the view put forward by the author in many of his memoirs, and as clearly stated on page 590 of Chapter XXXI.

Prof. W. L. Bragg also has lately (1921) been using very purely homogeneous X-rays for a similar purpose, derived by the preliminary reflection from a crystal of rock-salt of the rays from an already fairly



pure anticathodic source, such as the  $0.584 \times 10^{-8}$  cm. palladium anticathode. The undesirable remaining general radiations are got rid of by reflection from rock-salt at the correct glancing angle, and the intensity of the truly homogeneous component thus reflected can be measured with considerable accuracy. Then when this beam of truly homogeneous X-rays is allowed to fall upon a second crystal of rock-salt—or of any other substance under investigation—at the known glancing angle, the intensity of the reflected beam obtained from this second crystal affords a particularly valuable measure of the reflecting efficiency of the face. From a series of experiments of this kind it has been found possible to arrive at a theoretical formula for the intensity of the X-ray reflection from any plane of rock-salt or other substance worked with. The formula, for the reflecting power  $R$  of a face, which has been found most satisfactory by Prof. Bragg<sup>1</sup> is as follows:

$$R = \frac{N^2 \lambda^3}{2\mu \sin 2\theta} \cdot F^2 \frac{e^4}{m^2 c^4} \cdot \frac{1 + \cos^2 2\theta}{2} \cdot e^{-B \sin^2 \theta}.$$

It combines the results of Sir William and W. L. Bragg, of Darwin and Compton, and of Debye and Scherrer.<sup>2</sup> This formula, besides involving a number of constants the values of which are known—namely, the absorption coefficient  $\mu$  of the crystal, the number of atoms  $N$  per unit volume, the wave-length  $\lambda$  of the X-rays, the glancing angle of reflection  $\theta$ , the charge  $e$  and mass  $m$  of an electron, the velocity of light  $c$ , and a constant  $B$ —involves, in addition, a factor  $F$  the value of which depends on the arrangement of the electrons in the atom. By comparing the theoretical formula with the measurements obtained by experiment it is possible, since all the other constants are known, to determine this factor over a range of angles, and thus to obtain important information as to the arrangements of the electrons in and around the atom, especially concerning the positions of those comprising the outer shell. Up to the present (March 1921) the indications obtained in this manner are also in accord with the Lewis-Langmuir version of the atomic structure theory. The model of atom which agrees best with the observed values of  $F$  is one in which the electrons are supposed to be arranged on shells, and in oscillation about their mean positions, along a line joining them to the centre of the atom, with a total amplitude equal to their distance from the centre.

It is thus obvious that in the investigation of crystals by means of X-rays we have a powerful instrument of the richest promise for further discovery concerning the ultimate structure of matter, and with these latest most fascinating experiments this account of the results already achieved may well close.

<sup>1</sup> W. L. Bragg, R. W. James, and C. H. Bosanquet, *Phil. Mag.*, 1921, 41, 309.

<sup>2</sup> With reference to the method of X-ray analysis of Debye and Scherrer, in which crystal powder is used, Sir William Bragg has shown, in a paper read to the Physical Society on 8th April 1921, that crystals in the form of powder can be examined by the ionisation method. The powder is pasted on a flat surface and placed on the spectrometer table in the position ordinarily occupied by the face of a single crystal. A bulb current of 1 milliampere is sufficient to give satisfactory records.



## CHAPTER XXXIV

FEDOROV'S THEORY OF CUBIC AND HYPOHEXAGONAL TYPES AND OF THE CORRECT DESCRIPTIVE SETTING OF CRYSTALS; HIS METHOD OF CRYSTALLOCHEMICAL ANALYSIS—THEORY OF POPE AND BARLOW—MOSELEY'S LAW, ATOMIC NUMBER AND ATOMIC STRUCTURE

THE importance of choosing the correct mode of setting up a crystal for descriptive purposes has already been alluded to, and a brief account of the work of Fedorov, who has made a special study of the question, may be here given. The facts that the greater part of Fedorov's memoirs are in the Russian language, and that such as have been translated or abstracted in another language have suffered in the process and have not presented the complete case, besides the further fact that the ideas presented have changed somewhat in successive papers, have prevented the work of Fedorov receiving the attention which it undoubtedly merits. Only a bare outline can of necessity be given within the limits of a single chapter, of the leading ideas which serve as the groundwork of Fedorov's contributions to the theory of crystal structure and correct setting. But some account of Fedorov's theory of crystal structure has already been given in Chapter XXX. (page 567), and sufficient further data will be found here to be of practical use; for further details regarding both the theory and its application to practical examples, as well as for the equations for the transformation of crystal elements and indices from one setting to another, the reader is referred to the original papers and abstracts in the *Zeitschrift für Krystallographie*, and more especially to the memoir entitled "Allgemeinste Krystallisationsgesetze."<sup>1</sup>

**Parallelohedral Structure.**—According to Fedorov a crystalline substance may be regarded as built up of an immense number of small solid figures, similar and equal to each other, and of such a shape that when arranged in parallel position the whole of space is filled up, leaving no interstices whatever. Such geometrical figures are termed "parallelohedra," being bounded by pairs of parallel faces.

Parallelohedra are subdivisible into primary and secondary parallelohedra, the former possessing plane faces, and the latter being bounded either partially or wholly by curved faces. The number of varieties of the latter is obviously infinitely great; primary parallelohedra, on the other hand, are much less numerous, and moreover can be referred to five types. It is with these five types of parallelohedra that we have to deal in

<sup>1</sup> *Zeitschr. für Kryst.*, 1904, 38, 321-490.

crystalline structures, and they are in complete harmony with the space-lattices treated of in Chapter XXXI., and with the now accepted form of the Sohnckian point-system crystal-structure theory developed in that chapter and in Chapter XXX.

The five primary parallelohedra with plane faces are : (1) the cube, a triparallelohedron, as it is bounded by three pairs of parallel surfaces, and which is shown at *a* in Fig. 585 ; (2) the hexagonal prism, a tetraparallelohedron, being bounded by four pairs of parallel faces, as indicated at *b* in Fig. 585 ; (3) the rhombic dodecahedron, a hexaparallelohedron, there being six pairs of parallel faces, as represented at *c* in the figure ; (4) the elongated dodecahedron, having the same six planes and pairs of parallel faces as the rhombic dodecahedron, but elongated along one axis, taken as the vertical axis, as shown at *d* in Fig. 585 ; and (5) the cubo-octahedron, a cube truncated by the octahedron to the extent that each of the octahedral faces presents a regular hexagonal outline, thus forming a solid having seven pairs of parallel faces, and consequently a heptaparallelohedron, as illustrated at *e* in the figure.

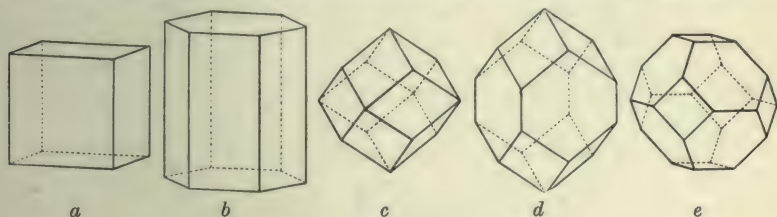


FIG. 585.—The Five Parallelohedra of Fedorov.

The elongated dodecahedron is indistinguishable from the rhombic dodecahedron either by number or disposition of faces, and may consequently for crystallographic purposes be regarded as an unessential variety of the latter, leaving us only with four essential parallelohedra, the **cube**, **dodecahedron**, **cubo-octahedron**, and **hexagonal prism**.

A crystalline medium may be regarded as built up of a great number of any one of these four parallelohedra, and it will then be said to have one of the structures **cubic**, **dodecahedral**, **octahedral**, or **prismatic**.

Now the first, second, and third all possess the symmetry of the cubic system, whilst the symmetry of the fourth is quite distinct. We may, therefore, divide crystals into two principal **types**, the **cubic** and the **hypo-hexagonal**, the former embracing all the three forms of cubic structure, and the latter the unique prismatic structure.

The cube is capable of being transformed by homogeneous deformation into a tetragonal, orthorhombic, or monoclinic prism ; also into a rhombohedron, or, the most general case, into the anorthic (triclinic) parallelepipedon. Each of these figures is a parallelohedron still, and a number of them may be packed together to fill space completely. The same holds good for the other three parallelohedra. Provided the deformation be homogeneous, a parallelohedron always remains a parallelohedron. From this it might at first sight appear that a crystal belonging

to any one of the seven systems and their 32 divisions or classes might possess any one of the four structures; but further consideration leads us to the conclusion that the choice is limited. For the symmetry of the parallelohedron must be consistent with the symmetry of the system and class to which the crystal belongs. It follows immediately from this that the prismatic structure is an impossible one for crystals of the cubic system, while crystals of the hexagonal system must necessarily possess that structure. Again, the four-fold, simple or alternating, axis of the classes of the tetragonal system is incompatible with the prismatic structure. Hence, cubic and tetragonal crystals must possess one of the first three structures, or, in other words, must belong to the **Cubic Type**, whereas hexagonal crystals must have the prismatic structure, and belong to the **Hypohexagonal Type**. As regards the elements of symmetry exhibited by the classes of the rhombohedral, orthorhombic, monoclinic, and anorthic (triclinic) systems, there is nothing incompatible with any of the four (appropriately homogeneously deformed) parallelohedra, and crystals belonging to these systems may belong to either the cubic or the hypohexagonal type. Rhombohedral (trigonal) crystals belonging to the cubic type, such as calcite, are termed trigonaloid to distinguish them. It will next be important to see how these four parallelohedra of Fedorov are related to the 14 space-lattices which we have accepted as the basis of all crystal structure, as given in Chapters XXX. and XXXI.

**Relations of Parallelohedra to Space-lattices.**—A crystalline medium is certainly not a continuous one, composed of solid parallelohedra without any vacant space. Hence, each of Fedorov's tiny parallelohedra does not really represent solid matter, but rather the field of influence of the structural unit placed at or around its centre. By field of influence of a unit is meant the space in which that unit exerts a paramount influence, and within which the matter of adjacent similar units never penetrates. It is obvious that by replacing a closely packed stack of cubes by points at their centres we obtain the cubic space-lattice of Bravais; and although perhaps not quite so obvious, it will be found on consideration that stacks of closely packed dodecahedra, cubo-octahedra, and hexagonal prisms, when treated similarly, give rise to the centred-face, centred-cube, and  $120^\circ$ -prism space-lattices respectively, Nos. 3, 2, and 6 of Chapter XXXI., as will be quite clear on referring to the descriptions of these space-lattices given in that chapter. Carrying out this operation on all the deformed parallelohedra, severally compatible with the various systems, we obtain in all 22 point-systems, each corresponding with a close-packed system of parallelohedra. Of these 22 point-systems some prove on examination to be identical. For instance, in the tetragonal system there are three possible parallelohedral structures, the hexahedral, dodecahedral, and heptahedral; the first corresponds to the simple tetragonal lattice, Fig. 455, page 583, whilst the second and third correspond with one and the same lattice, the centred tetragonal lattice, Fig. 456 on page 583. It is by reason of such identities that the 22 systems of parallelohedra are connected with the 14 space-lattices.

If for any particular crystal the volume of the parallelohedron be



taken proportional to the molecular volume, then the distances between the centres of parallelehedra in specific directions represent the molecular distance ratios (topic axial ratios) for those directions.

**The Correct Setting of Crystals.**—The setting up of a crystal for descriptive purposes, that is, the choice of which direction shall be called the vertical axis and which other directions the lateral axes, can hardly be said to have been hitherto founded on any definite principles. Such rules as assigning the indices (100), (010), and (001) to the three planes of symmetry in the case of an orthorhombic crystal, or the indices (010) to the unique symmetry plane of a monoclinic crystal, are, of course, of great value as far as they go, and satisfy the purposes of classification; but they still leave considerable latitude, as to which of the three planes of symmetry shall be (100) and which (001) for instance, or which direction in the unique plane of symmetry shall be the vertical axis, and in both cases the elements (and in the former case the order of the three planes) depend on what plane shall be considered as the parametral one, for the choice of which the latitude is even greater. Indeed, the choice is usually more or less arbitrary from the structural point of view now under discussion. Owing to this absence of any guiding principle it is not surprising to find different authors setting up the same crystalline substance in different ways, while based on the same order (system and class) of symmetry with respect to which all agree. The habit may appear to justify the setting in each case, but the habit is often dependent on the local circumstances of growth of the crystal; for the same substance may display different habits in different crops or preparations. Moreover, it is often observed that in the description of triclinic crystals very high degrees of anorthism are given, and in the case of monoclinic crystals high inclination of the inclined axis; thus, for example, the latter angle  $\beta$  is given in one case which recently came under the author's notice as  $28^\circ 27'$  or  $151^\circ 33'$ . Now, it is extremely unlikely that two of the principal directions in a crystal should deviate so greatly from  $90^\circ$  in the case of a crystal of cubic type, or from  $60^\circ$  in the case of a hypo-hexagonal crystal. It has been the object of Fedorov to discover some true guiding principle on which the correct setting can be attained, and the following is a brief account of his methods and of the ideas on which he bases them, for a discussion of which the foregoing description of Fedorov's views of crystal structure, and the discussion in Chapter XXX., page 567, will have paved the way.

(1) All crystals are divisible, according to Fedorov, into two **Types**, **Cubic** and **Hypo-hexagonal**, corresponding to the four structures previously enumerated. This follows deductively from his theory of crystal structure. It should be emphasised that crystals of the rhombohedral, orthorhombic, monoclinic, and anorthic systems may belong to the hypo-hexagonal type, as well as to the cubic type, that is, to either the one or the other, and their forms may, therefore, be represented by four indices.

(2) All crystals are either pseudo-tetragonal or pseudo-hexagonal in the wider sense, that is, when differences up to  $20^\circ$  are included. This

principle was arrived at by Fedorov from an examination of a great part of the published crystallographic data. The greater the variation from the ideal angles  $90^\circ$  and  $60^\circ$ , the fewer are the examples actually found.

It may perhaps be here suggested that as the terms pseudo-tetragonal and pseudo-hexagonal are already employed for those cases where the deviation is one of minutes only,—as in the cases of the pseudo-hexagonal (orthorhombic) alkali sulphates and selenates fully described in previous chapters, where the differences of angle from true hexagonal symmetry ( $60^\circ$ ) are less than half a degree and often less than ten minutes only,—it would be better to employ the terms tetragonaloidal and hexagonaloidal for the wider sense (including differences up to  $20^\circ$ ) meant by Fedorov.

Directly derivable from these two principles are the following subsidiary ones marked (3), (4), and (5). Since crystals are either tetragonaloidal or hexagonaloidal, it results that the chief characteristic is the ratio of the principal axis to one of the horizontal subsidiary axes. Where this value is equal to unity, the crystal is said to be an isotropic complex, and the angle between the basal plane and the primary pyramid is  $54^\circ 44'$  and  $49^\circ 6\frac{1}{2}'$  respectively. When the ratio is greater than unity, the angle is increased and the crystal is termed **positive**. When the reverse holds, the crystal is **negative**.

(3) From the theory of crystal structure it follows that in a positive crystal (Fig. 586) the points of the network are most densely massed in a **singular plane** (the basal plane in Fig. 586), in which will therefore lie the directions of maximum cohesion; these are the directions of most intense growth, hence the crystal will be characterised by a tabular habit and a cleavage parallel to this singular plane.

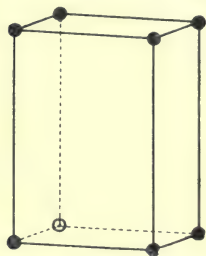


FIG. 586.—Elementary Cell of Positive Crystal.

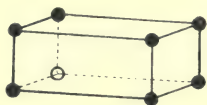


FIG. 587.—Elementary Cell of Negative Crystal.

(4) Conversely it follows that in negative crystals (Fig. 587) there is a **singular direction** (parallel to the vertical edges in Fig. 587) of maximum cohesion and most intense growth; we therefore meet with a prismatic

habit (elongated), and cleavages, if any, are prismatic also, that is, lie in the zone the axis of which is the singular direction referred to. It will be observed that the habits of the crystals are the converse of those of their structural parallelepipeda. But fortuitous circumstances of growth frequently mask this characteristic habit by bringing about modifications.

(5) Again, from geometrical considerations, it is easy to prove that in positive crystals the forms (other than the primary pyramids and domes) which have the greatest reticular density are negative forms, that is, forms making smaller angles with the base than the primary forms. The reverse holds for negative crystals, for the forms making greater angles with the base now have the greater reticular density.

**The method of obtaining the correct setting on the lines of these**



five principles is as follows : An accurate stereographic projection is made on one of the stereographic nets, such as that of Fedorov himself, or the still more convenient one as regards size (2·5 inches radius) of Hutchinson described in Chapter VI., and reproduced in Fig. 52 (p. 104). It must then be noted whether the angles between the principal forms approximate to  $90^\circ$  or to  $60^\circ$ , also whether the primary pyramids and domes agree better with a development corresponding to a tetragonal or to a hexagonal pyramid. Attention may also be paid to the angular distances between cleavage forms, if any exist, and the other principal forms, with a view to the discovery of positive or negative character. By inspection of this kind one is usually able to discriminate whether the crystal belongs to the cubic or to the hypohexagonal type, and in the former case, may indeed obtain some insight into the structure, as to whether it is cubic, dodecahedral, or octahedral. The most likely setting having been selected in this way, its value is then estimated in the following manner. The reticular density is calculated of all the observed parallel pairs of faces, as also that for any possible faces not actually present, which, from having simple indices, may *a priori* be predicted to have fairly high densities ; if the density of one of the faces be taken as unity, the calculation of the relative densities of the remainder may be fairly rapidly made to a sufficient degree of accuracy by a graphical method based on the stereographic projection.

When all the observed forms are actually the forms of greatest possible reticular density, the form development may be regarded as ideal, and the setting as fully established. But when there are absent certain forms of reticular density greater than some of those actually present, one should proceed to estimate the relative value of the setting, compared with the ideal setting, by summing the squares of the densities (1) of the observed pairs of faces, (2) of an equal number of faces possessing as high a reticular density as possible ; dividing the former by the latter we obtain a decimal fraction which is the nearer to unity the greater the approach to ideal form development, and which, if the latter be really present, actually becomes equal to unity. The same process must be carried out for any other setting considered likely to be ideal. The difference between the values of the decimal fraction, obtained for the different alternative settings of the same crystal, is usually so considerable that no difficulty attends the selection of the correct setting. The value for the correct setting will generally be greater than 0·9, whilst for incorrect settings a much lower value, often as low as 0·5, is obtained. In a crystal of the cubic type, the reticular density of a particular face will, generally speaking, vary according as the structure is cubic, dodecahedral, or octahedral, and it is by means of this property that a critical comparison of the observed forms with ideal form development for each type of structure enables one to discriminate between the three possibilities. In practice, the cubic structure is found to preponderate greatly.

Just as with an insufficiency of form development it is often impossible to determine all the elements of a crystal belonging to one of the less symmetrical systems, so it is equally true that this may also prevent the discrimination or selection of the correct setting. It may also be remarked



that forms which either occur rarely, or are vicarious replacements (vicinal faces), are of little value ; for they are not so much characteristic indicators of form development as of changes in the external conditions of crystallisation. It is a good rule to take only those forms into account which are present, say, in more than half of the crystals investigated. It is interesting to note, in connection with the work of Miers on vicinal faces and his explanation of them as described in Chapter XXIV., that when an old setting has been proved to be incorrect, the indices of rare forms become often still more complicated (higher index numbers) for the ideal setting, the faces then approximating more closely to those of a possible form with low indices, not actually observed, but probably replaced by the high-index vicinal faces, in the manner which has been made so clear by Miers.

Sufficient will now have been said to afford some insight into the important and highly interesting views of Fedorov. It is much too early to express an opinion as to their complete validity, for only extensive further experimental work can decide. But it is for the very reason that in all future investigations Fedorov's method of arriving at a proper setting of the crystal should be tested, that this chapter has been written. To the author, the wide limits of  $20^\circ$ , for inclusion in the cubic or the hypohexagonal type, appear very wide, and it is here that the test of further work is mostly required. In narrower cases like the sulphates and selenates of the alkalis, involving only a few minutes of deformation from truly hexagonal symmetry, the pseudo-hexagonal (and therefore certainly hypohexagonal in Fedorov's sense) character is unmistakable, and the author has unreservedly adopted Fedorov's method as regards the structural constants, and has given the molecular distance ratios of these orthorhombic salts on the basis of a pseudo-hexagonal structure (see table of these constants on page 641 at the close of Chapter XXXII.).

An example of the use of Fedorov's method is given by Mr. T. V. Barker (who learnt it direct in Prof. Fedorov's laboratory in Petrograd) and Miss Mary W. Porter<sup>1</sup> in a memoir just published concerning the crystal characters of a number of related complex organic substances. A two-circle goniometer (latest 1920 pattern, Fig. 367, page 455) was used, and is recommended as especially useful for the rapid measurement of laboratory products, since only one adjustment of the crystal is necessary. The results were plotted on a Fedorov stereographic net, and the crystal system, if not immediately obvious, was deduced from the zonal angles, graphically determined with the help of the three-point compass and stereographic net. The crystal-facial indices were determined graphically with the help of the gnomonic projection, and the axial ratios both by the usual method of the solution of spherical triangles and by V. Goldschmidt's method (pages 457 and 473) based on the gnomonic projection. The drawings of the crystals were made from the gnomonic projection by the method described on page 484.

Perhaps the best mode of illustrating the difficulty of following Fedorov the whole way, and incidentally of throwing more light on his method, will be to consider the case of the setting of the important monoclinic

<sup>1</sup> *Journ. Chem. Soc.*, 1920, 117, 1303.

series of isomorphous double sulphates and selenates,  $R_2M\left(\begin{smallmatrix} S \\ Se \end{smallmatrix} O_4\right)_2 \cdot 6H_2O$ , of which the member ammonium magnesium sulphate was studied in detail in Chapter XVII. as a typical example of monoclinic symmetry.

The "setting" of the crystals of the salts of this series has been gone carefully into by Fedorov.<sup>1</sup> The setting employed by the author,<sup>2</sup> which will be clearly apparent from Fig. 215, the drawing of ammonium magnesium sulphate, and Fig. 216, the general stereographic projection for the whole series, both given on page 258, is that which was given by Murmann and Rotter, and, as it is the most natural one in precise keeping with the undoubtedly holohedral monoclinic symmetry of the crystals, was adopted by the author in the absence of any opposing reason.

It has been shown by the author that this setting is preferable to that proposed by Wulff,<sup>3</sup> who takes the faces of the form  $r'\{201\}$  as those of the basal pinakoid  $\{001\}$ , when the development of faces throughout the whole series is generally considered, and Fedorov confirms this preference from the standpoint of the rule regarding reticular density. Both the settings of Wulff and of the author agree with monoclinic symmetry, but Wulff rotates the crystal about the symmetry axis until  $r'$  becomes the basal plane instead of  $c$ , both these planes being in the orthozone at right angles to the symmetry plane.

Fedorov, however, proposes yet another setting, which he finds to agree better with the rule of reticular density. But it is, in the opinion of the author, much to its disadvantage that the reason for it is really based on the peculiar form of the geometrical theory of crystal structure which has been advanced by Fedorov, and particularly on that part of it which is not so firmly grounded as that which refers only to the derivation of the 230 possible point-systems concerned in crystal structure; this more hypothetical part refers to the nature of what the points represent, and to Fedorov's idea that all crystals are of either cubic or hexagonal type or of one of those types more or less deformed, which he terms pseudo-cubic and pseudo-hexagonal or hexagonaloid. Fedorov retains the same vertical axis as the author in his proposed setting, but rotates the crystal for  $180^\circ$  around it. If, instead of arranging the stereographic projection of a monoclinic crystal as usual in this country, projected on the symmetry plane, as is done in Fig. 216 on page 258, we retain the method adopted for the other crystal systems, of making the primitive circle of the projection the prism and primary pinakoid zone, with the poles (100) and  $(\bar{1}00)$  in front and behind and (010) and  $(0\bar{1}0)$  right and left respectively, a method which is often adopted in Germany for monoclinic crystals, we have the projection given in Fig. 588. The setting of Fedorov is represented in Fig. 589, which is evidently the same as Fig. 588 rotated for  $180^\circ$  in the plane of the paper, that is, about the vertical axis represented in plan by the centre of the projection, which in a

<sup>1</sup> *Zeitschr. für Kryst.*, 1909, 46, 258.

<sup>2</sup> *Journ. Chem. Soc.*, 1893, 63, 337; Fig. 1, p. 343, is the original of the stereographic projection reproduced in Fig. 216 on page 258 of this book.

<sup>3</sup> G. Wulff, *Zeitschr. für Kryst.*, 1901, 34, 486.

rhombic crystal would be the position of the facial pole of the basal plane,  $c$  (001), which pole, however, is now displaced forwards in Fig. 588 by the angle of monoclinic tilt  $16^\circ 50'$ , and in Fig. 589 to the same extent backwards. In both figures the plane of symmetry is represented by the diameter parallel to the longer edges of the page.

While thus Fedorov merely alters the author's setting by this rotation for  $180^\circ$ , bringing what was the back of the crystal to the front and *vice versa*, he regards the various poles from an altogether different standpoint. He ignores the monoclinic symmetry, except as being a deformation in one direction, and states that the crystal complex appears to be a

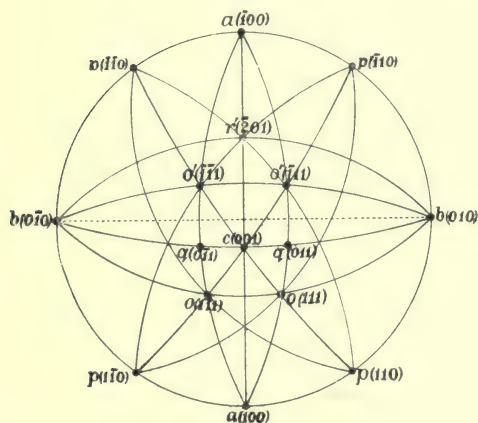


FIG. 588.—Tutton's Setting.

Alternative Settings for Double Sulphates with  $6\text{H}_2\text{O}$ .

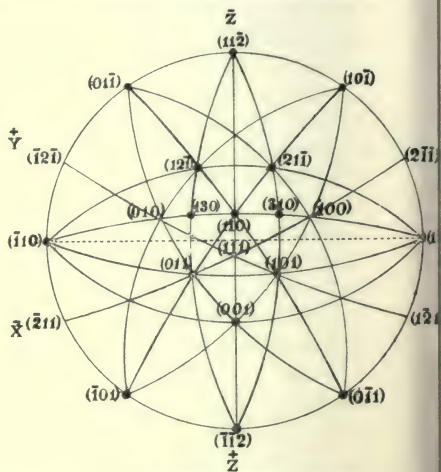


FIG. 589.—Fedorov's Setting.

hexagonaloid one of cubic type, that is, one of trigonaloid character, which he expresses, in accordance with a method of concise symbols<sup>1</sup> which he employs, thus :

$$\begin{array}{c} 3o ; +13 \\ 47\frac{1}{2} \\ -5\frac{1}{2} \end{array}$$

The letter  $o$  in the top line indicates the octahedral main structure ; the 3 in front of it represents the trigonaloid character, which is similar to the rhombohedral one of calcite, but considerably deformed (in one direction) from the form of the regular rhombohedron ; the +13 signifies

<sup>1</sup> T. V. Barker and Miss M. W. Porter (*loc. cit.*) describe the Fedorov "complex-symbol" as an expression indicating simultaneously the type of structure and the characteristic angles (if necessary, after a suitable homogeneous deformation or shear). The initial term of the symbol is the number 6, 4, or 3, according as the crystal is of hexagonal, tetragonal, or trigonal (rhombohedral) type. This is followed by  $h$ ,  $o$ , or  $d$ , indicating hexahedral (a simple lattice), octahedral (a centred lattice), or dodecahedral (a face-centred lattice). All the remaining terms of the symbol are degrees of arc, which serve to characterise the crystal species, as described above in the text. The main use of the complex-symbol is, on account of its conciseness, for the purpose of tabulation and classification in the *Fedorov Dictionary of the Crystal-Kingdom* (see page 733).



the number of degrees of monoclinic deformation, on the + side of the trigonal axis  $Z$ , that is, the angle between the centre of the projection, which in a truly trigonal crystal like calcite is occupied by the pole (111), and the actual position of the pole of the possible face which is analogous to (111) on the deformed crystal. The central number  $47\frac{1}{2}$  represents the number of degrees in the principal angle (111) : (001), that is, between the basal plane and one of the faces of the primary rhombohedron, on the supposition of trigonal character and after imaginary re-deformation of (111) back to true trigonal symmetry, that is, to the centre. The lower number  $-5\frac{1}{2}$  represents the angular deviation from  $30^\circ$  of the poles on the primitive circle, that is, of the poles which in trigonal symmetry would correspond to  $(\bar{1}01)$  and  $(\bar{1}\bar{1}2)$ ; these are adjacent faces of the two varieties of hexagonal prism in a truly trigonal crystal, and are in the latter  $30^\circ$  apart, but in the neighbourhood of  $35\frac{1}{2}^\circ$  (the angle  $ap$ ) in this series of double sulphates ( $35^\circ 16'$  in ammonium magnesium sulphate).

Fedorov gives the following transformation equations (*loc. cit.*, page 259) for the conversion of the indices  $p_1, p_2, p_3$ , of any face according to the monoclinic setting of the author, to the corresponding indices  $q_1, q_2, q_3$ , according to Fedorov's trigonaloid setting :

$$q_1 : q_2 : q_3 = p_1 - p_2 + 2p_3 : p_1 + p_2 + 2p_3 : -2p_1,$$

or the determinants :

$$\begin{vmatrix} 1 & \bar{1} & 2 \\ 1 & 1 & 2 \\ \bar{2} & & \end{vmatrix}$$

The indices of the principal faces according to the two settings are given below, those of the author's setting being in brackets as usual, and those of Fedorov not, in order to distinguish them :

$$\begin{aligned} c \text{ (001)} &= 110, \quad r' \text{ (}\bar{2}01\text{)} = 001, \quad a \text{ (100)} = 11\bar{2}, \quad b \text{ (010)} = \bar{1}10, \\ q \text{ (011)} &= 130, \quad o' \text{ (}\bar{1}11\text{)} = 011, \quad p \text{ (110)} = 01\bar{1}. \end{aligned}$$

It will be clear that the  $r'$ -face of the author's setting becomes the rhombohedron face (001) [the  $r$  (001) of calcite], and the  $c$ -face becomes the face (110) [the  $e$  (110) of calcite]. The setting of Fedorov, thus regarded as a monoclinically deformed rhombohedral one, corresponds to a similarly deformed rhombohedral space-lattice, while the setting of the author corresponds to the second (pinakoidal) monoclinic space-lattice, No. 13 (Fig. 468 on page 587).

The author regards this deformation idea, in cases like this where the difference from  $30^\circ$  is as much as  $5\frac{1}{2}^\circ$  and the displacement of (111) from the centre no less than  $13^\circ$ , as an unnecessary complication, and one which is not likely to be followed in actual practice by chemists or crystallographers desirous of making use of the great advantages of crystallo-chemical analysis. Moreover, it will be obvious that if we follow Fedorov all the way, and accept the assumption of a deformed trigonal symmetry, the following important forms or faces are missing, indicated on Fig. 589 by their indices, but without pole-dots : {111} the basal plane ; four of the six faces of the hexagonal prism of the first order {2 $\bar{1}$ 1}, for only two, (11 $\bar{2}$ ) and ( $\bar{1}$ 12), are generally developed, which

are the  $a$ -faces (100) and ( $\bar{1}00$ ) of the author's monoclinic setting, the other four faces, ( $2\bar{1}\bar{1}$ ), ( $\bar{1}21$ ), ( $21\bar{1}$ ), and ( $\bar{1}2\bar{1}$ ), having only been seen developed to a measurable extent on one or two crystals of ten of the 59 investigated salts of the series as the minute faces  $p'''$  (namely, on KCu-, RbCu-, CsCu-, AmCu-, RbCd-, CsCd-, AmCd-, AmMn-, and AmMg-sulphates, and on RbCu-selenate); and two of the three faces of the primary rhombohedron itself {100}, for only one, (001), is present, while (010) and (100) are generally entirely absent, and have only been seen by the author as minute faces (the  $m$ -faces) on six of the 59 salts of the series investigated, namely, KNi-, RbCu-, and CsCd-sulphates, and KCu-, CsCu-, and AmCo-selenates. Further, which is even more significant, while it is true that all six faces of the hexagonal prism of the second order {10 $\bar{1}$ } are developed, four of them are the largely and generally predominatingly developed faces of the primary prism  $p$  {110} of the author's monoclinic setting, while the other two are very small and frequently absent faces of the clinopinakoid  $b$  {010}; that is, two clearly different and very unequally developed forms make up the six faces which Fedorov proposes to consider as a hexagonaloid prism. Again, the cleavage is only developed parallel to one plane, that of the pair of parallel faces of  $r'$  {201}, that is, only parallel to one of the three planes of the pseudo-rhombohedron of Fedorov.

Thus, while it may be true that the faces of the pseudo-rhombohedron possess the maximum reticular density, still there appear to be so many deficiencies as regards development of primary planes, either as faces or cleavage planes, that the author much prefers to accept the simple and obvious monoclinic symmetry of both faces and cleavage as determinative of the setting; and as Wulff's setting is still less to be preferred, both for the reasons given by the author and for the additional ones also advanced by Fedorov, it is considered preferable to retain the setting which has been adopted throughout all these investigations.

If a clearly hexagonal habit were presented, and all the essential faces well developed, such as in the cases of the simple rhombic sulphates and selenates of the alkalis, where the differences from exactly  $30^\circ$  are only a few minutes, the presence of a pseudo-hexagonal space-lattice could with reason be accepted, and in the descriptions of those salts the author has given the dimensions of the elementary cells of the space-lattice on such an assumption. But in this monoclinic series of double salts such is not the case.

**Crystallo-chemical Analysis.**—It is understood from Mr. T. V. Barker—who spent a considerable time with Prof. Fedorov in Petrograd, and to whom the author is also indebted in connection with the account of Fedorov's theory earlier in this chapter—that Prof. Fedorov had, by the time of the commencement of the war in August 1914, almost completely worked through and determined the correct setting of all the substances, over ten thousand in number, hitherto crystallographically investigated. For rapid work (two hours sufficing for an unknown substance to be sufficiently worked out) he used his two-circle goniometer (Fig. 368, described on page 456). He had also devised a method of measurement and calculation which he termed the System of Bipolar Co-ordinates, dependent on the



use of two fundamental faces as pole-faces, and in which the necessary calculations reduce themselves to the addition or subtraction of the cotangents of measured angles. An account of the method was given by Fedorov<sup>1</sup> in the year 1914 in a memoir in the *Zeitschrift für Krystallographie*, and a still more detailed account had already been given by Mr. Barker<sup>2</sup> in an abstract (of a Russian memoir by Fedorov) published in the same periodical in the year 1909. While interesting, and capable of rapid results in the hands of an expert, the method effects in the end nothing beyond what can be reached by the ordinary method of two-circle goniometry.

Fedorov had drawn up the vast material which he had collected into an index or table, which is termed the *Dictionary of the Crystal-Kingdom*, on the principles enunciated in this chapter, namely, on the basis of four structures belonging to the two types, cubic and hypohexagonal, and arranged the numerous substances belonging to each in their order, starting from the most negative and ending with the most positive, and describing them progressively by means of the concise complex-symbols described on page 730. Moreover, what is more astonishing, he had succeeded in determining and identifying the majority of a large number of substances the crystals of which had been collected by Mr. Barker from various crystallographers who had measured them, and had been sent out by him to Prof. Fedorov at Petrograd, without either their names or chemical formulæ appearing on the labels of the bottles, but merely a reference number, just as if the substances had been unknown new ones.

Hence, Fedorov would appear to have discovered a purely crystallographic method of analysis which we may term "**crystallo-chemical analysis**," which is of real practical value. The publication of his index table, the *Dictionary of the Crystal-Kingdom*, was delayed by the war and the disorder in Russia, and now the sad news of his death, during the troubles following the Russian revolution, forbids us to continue to anticipate its publication by the master himself. It is hoped, however, that the Dictionary will eventually be published by the Petrograd Academy of Science, and thereby so remarkable and laborious a work saved from destruction and oblivion. In the meantime it is of great interest to record such considerable progress in the identification of crystalline substances entirely by their crystal morphology.

**Theory of Pope and Barlow.**—In the year 1906 a theory of crystal structure was advanced by Sir William Pope and Mr. W. Barlow.<sup>3</sup> The previous valuable work of the latter investigator on the geometry of homogeneous structures has already been discussed in Chapter XXX. Like Fedorov, Pope and Barlow also regard the whole volume occupied by a crystalline structure as partitioned out into polyhedra, which they conceive to be derived by compression of a closely packed assemblage of deformable but incompressible elastic spheres, the "spheres of influence" of the chemical atoms. The most original feature of their theory is, however, that the volumes of the spheres, or rather of the polyhedra, are

<sup>1</sup> *Zeitschr. für Kryst.*, 1914, 54, 29.

<sup>2</sup> *Ibid.*, 1909, 46, 202.

<sup>3</sup> *Journ. Chem. Soc.*, 1906, 89, 1675; 1907, 91, 1150; and 1908, 93, 1528.



assumed to be proportional to the chemical valency of the atoms which the spheres represent; the volume, for instance, of the sphere of influence of a carbon atom is supposed to be four times that of a hydrogen or chlorine atom present in the same molecule. They substitute the sum of the valencies of the atoms present in the molecule—the “valency volume”—for the molecular volume in the formulæ given in Chapter XXXI. for the molecular distance ratios, thus obtaining “equivalence parameters.” The theory does not concern itself with the relationships in isomorphous series (which are expressed by the molecular distance ratios), nor with the phenomena of the relative densities and molecular volumes of crystals.

In confirmation of Fedorov, Pope and Barlow first show that there are two methods of closely packing equal spheres, which give rise respectively to a cubic and to a hexagonal crystal structure, the latter endowed with a specific axial ratio;  $a:c = 1:1.6330$  or  $1:1.4142$ , there being two alternatives; and that the crystalline chemical elements, of which the atomic spheres of influence must obviously be equal, practically all crystallise either in the cubic or the hexagonal (or trigonal) system, and in the latter case with approximations to one or other of the two alternative specific axial ratios referred to. Thus beryllium and magnesium approximate to the  $c$ -value 1.6330, and zinc, cadmium, arsenic, antimony, bismuth, and tellurium to the  $c$ -value 1.4142 (*loc. cit.*, 1907, pages 1157 and 1161). This result, however, is quite independent of their valency volume theory.

The essence of their theory has perhaps been best stated by Pope in a *Report on the Progress of Crystallography* published by the Chemical Society in the year 1909, and the following quotation expresses the salient propositions. They regard “the whole of the volume occupied by a crystalline structure as partitioned out into polyhedra, which lie packed together in such a manner as to fill the whole of that volume without interstices. The polyhedra can be so selected that each represents the habitat of one component atom of the material, and are termed the spheres of atomic influence of the constituent atoms. Up to this point no assumption is made other than that clearly indicated by the result of crystallographic measurements, namely, that each atom present in a crystalline structure exerts a distinct morphological effect—or, what is the same thing, appropriates a certain definite volume. The assumption is next made that the crystalline structure, which is resolvable into individual molecules and ultimately into individual atoms, exists as such by reason of equilibrium set up between opposing attractive and repulsive forces operating between the component atoms, and that this equilibrium results in the polyhedra representing the spheres of atomic influence assuming shapes which are as nearly as possible spherical. . . . The polyhedra thus arrived at may be regarded as derived by compression of a close-packed assemblage of deformable, incompressible elastic spheres, the compression sufficing for the practical extinction of the interstitial space. When such an assemblage is released from pressure it is evident that in place of polyhedra, the shapes of which approximate as closely as possible to the spherical, closely packed spheres are presented; the dis-

tances between the sphere centres can be substantially in the same ratios as the distances between the centres of the corresponding polyhedra in the unexpanded mass, and the equilibrium condition of maximum sphericity of the polyhedra will be presented in the expanded mass of spheres by the existence of the maximum number of contacts between spheres. The whole method of treating the primary assumption thus resolves itself into finding close-packed assemblages of spheres of various sizes representing by their relative volumes the spheres of influence of the component atoms of any particular crystalline structure. . . . The conclusion is that the volumes appropriated by the polyhedra representing the spheres of atomic influence in any crystalline structure are approximately proportional to the numbers representing the valencies of the respective elements concerned. In every case hitherto studied the valency thus exhibited by an element is the lowest which its chemical behaviour assigns to it; this valency is conveniently distinguished as the fundamental valency of the element. The law thus enunciated is termed the law of valency volumes."

A considerable amount of evidence has been presented by its proposers which they consider to support their theory. It would appear at first sight to express the crystallographic relationships of the elements in the horizontal series of the periodic classification of Mendeléeff, the series of seven elements of each period regularly progressing in valency. But it is expressly stipulated that not the usual, but the minimum, valency is concerned, which at once modifies the impression. Moreover, it does not by means of its equivalence parameters (which show less than one per cent. of change in the group of alkali sulphates) account for the further undoubted progression of the vertical groups of the periodic table, the family groups of like valency but growing atomic weight and volume. These relationships, however, have been shown in previous chapters to be clearly expressed by the molecular distance ratios (which show ten per cent. of change), based on the accurate quantitative determinations of molecular weight, relative density, and morphological crystal elements; and the underlying cause of this very real progression exhibited by the members of an isomorphous series has been elucidated and explained by the remarkable results of Moseley, to be presently described.

Before going further with the discussion of the valency volume theory we may with advantage take stock of the position indubitably reached as the result of researches absolutely incontrovertible, even before the advent of the X-ray method of crystal analysis. It is clear that the four following conclusions have been definitely established: (1) Each atom of the molecule of the crystal substance possesses its own individual domain throughout which it exerts predominant influence; (2) the interchangeable analogous atoms in isomorphous series occupy similar relative positions in the respective structures; (3) the scheme of structure, style of architecture, type of space-lattice of the crystals of the members of isomorphous series of strictly analogous composition are identical; (4) the volumes and dimensions of the similar parallelepipedal unit-cells of the space-lattices of the various members of the isomorphous series formed by strictly comparable family-group elements (the inner "eutropic" series)



are relatively expressed by the molecular volumes and molecular distance (topic axial) ratios.

We thus definitely apportion the whole of the space in the crystal substance among the various atoms, assigning to each atom a portion of space throughout which its influence is paramount. The volumes occupied by the atoms of different elements of similar valency in their isomorphous compounds, such as those of potassium, rubidium, and caesium, or of sulphur and selenium, or of chlorine, bromine, and iodine, cannot possibly be the same, however. For the experimental evidence is emphatic that the total volume of the elementary parallelepipedon of the space-lattice structure is considerably increased as we ascend the series. The total change of volume is expressed by that of the molecular volume, while the directional change is expressed by the alteration of the molecular distance ratios; and the external crystallographic effect is expressed by the slight alteration of the crystal angles, in accordance with the law of progression with the atomic weight<sup>1</sup> or atomic number of the interchangeable elements.

The impossibility of accepting the theory of valency volumes of Barlow and Pope is clinched by the difficulty afforded by the remarkable behaviour of the ammonium compounds. The interchange of the five atoms of the ammonium group  $\text{NH}_4$  for a single atom of an alkali metal has been shown at the conclusion of Chapter XXXII. (page 642) to be remarkably slight, the replacement of potassium by ammonium, in fact, only calling forth almost precisely the same amount of change of molecular volume and molecular distance ratios as when rubidium is interchanged for potassium, and the replacement of rubidium by ammonium actually scarcely altering the volume and dimensions of the unit cell at all, the rubidium and ammonium salts being practically isostructural, whereas a doubling of the volume ought to occur when potassium or rubidium is replaced by ammonium if the valency volume theory be correct, as the sum of the fundamental valencies of  $\text{K}_2\text{SO}_4$  or  $\text{Rb}_2\text{SO}_4$  is 12, while that of  $(\text{NH}_4)_2\text{SO}_4$  is at least 24 (assuming nitrogen to be only triadic).

The following further discussion of the case of the ammonium salts, and of their bearing, and that of other researches, on the valency volume theory, is abbreviated from a memoir of the author communicated to the Royal Society in November 1916, and expresses the author's views very clearly (*Proc. Roy. Soc.*, 1917, vol. 93, p. 72).

For a series of isomorphous salts, such as the rhombic normal sulphates of the alkali-metallic family group of the periodic classification,  $\text{R}_2\text{SO}_4$ , where R may be potassium, rubidium, or caesium, there can be no possible

<sup>1</sup> Instead of "atomic weights" ( $\text{K}=38.85$ ,  $\text{Rb}=84.9$ ,  $\text{Cs}=131.9$ , and  $\text{Rb}-\text{K}=46$ ,  $\text{Cs}-\text{Rb}=47$ ,  $\text{Cs}-\text{K}=93$  or twice 46), we may substitute with equal validity "atomic numbers" (the numbers of the elements according to their sequence in the Periodic Table). For the atomic numbers of K, Rb, and Cs are 19, 37, and 55, and their differences are similarly related,  $\text{Rb}-\text{K}=18$ ,  $\text{Cs}-\text{Rb}=18$ , and  $\text{Cs}-\text{K}=36$  or twice 18. Indeed, it is probable that there is an intimate connection between this crystallographic law of the author and the law of Moseley, that the properties of an element are defined by the atomic number, which is equal to the number of units of positive electrical charge in the atomic nucleus, and to the number of the surrounding negative electrons.



doubt that the type of structure, that is of space-lattice, is identical. Its symmetry is the same for all the members of the group, but the dimensions of the elementary cell vary progressively with the atomic weight or atomic number of the interchangeable alkali metals; and correspondingly the interfacial angles also differ slightly and progressively, in accordance with very definite rules which have been established by the author (see page 381, and also Chapter LIV. on "Isomorphism").

When, however, we introduce the radicle ammonium,  $\text{NH}_4$ , instead of an alkali metal, and produce the isomorphous ammonium salt, the possibility has been suggested that the case may not be strictly comparable with the substitution of rubidium or cæsium for potassium. It is just conceivable that the observed similarity of symmetry and crystal angles may be accompanied by a considerable opening up of the structure, such as, for instance, by the introduction of the extra atoms of nitrogen and hydrogen in the form of new layers. That is, it might be a case of a very different sort of structure being produced as regards dimensions and arrangement, but outwardly conforming to the same type of rhombic symmetry, with a fortuitous close similarity in external crystal angles. Although, however, this is a possibility, it is highly improbable. It is true that the quality of the isomorphism of ammonium sulphate is so far different from that between potassium, rubidium, and cæsium sulphates as not to be subject to the law of progression with the atomic weight or atomic number of the metal, for we are now dealing with a non-metallic radicle group  $\text{NH}_4$ . The case is defined by saying that the ammonium salt, while truly isomorphous, does not belong to the exclusive "eutropic" group of the metallic salts, the term eutropism having been applied to the isomorphism of strictly analogous members of the group (their interchangeable elements belonging to the same family group of the periodic classification), which follow the law of progression with the atomic weight or atomic number of the interchangeable constituents both as regards morphological and physical (optical and other) constants.

But the author has shown that although the ammonium salt is not eutropic with the salts of the alkali metals, its molecular volume and topic axial ratios are indeed strictly comparable with those of the alkali metallic salts. That the ammonium salt is truly isomorphous with the alkali-metallic salts is strikingly shown by the fact that not only are the types of symmetry identical and the axial ratios very close (see table on page 641), but the average change of angle (mean for 37 measured angles) on replacing potassium by ammonium is not even quite so great as when potassium is replaced by cæsium, and the maximum change of interfacial angle follows the same rule. The angular change on substituting ammonium for potassium is, however, naturally greater than when rubidium is introduced instead of potassium, for this latter (Rb) replacement gives rise to only half as much change of angle as when cæsium is introduced for potassium, in accordance with the law of progression for the alkali metals, which law is very beautifully and directly expressed by this fact. To make the point clear, the actual figures for the sulphates are given in the following short table. It should be remembered that the difference

of atomic weight or of atomic number between K and Cs is just double that between K and Rb.

AVERAGE AND MAXIMUM ANGULAR CHANGES.

	Average Change.	Maximum Change.
For replacement of K in $K_2SO_4$ by Rb .	0° 9'	0° 26'
"      "      " $NH_4$	0 14	0 38
"      "      "      Cs .	0 16	0 50

Precisely similar facts are shown in the monoclinic double sulphate and selenate series, in which the angular changes are much larger; the precision with which the average and maximum changes for the caesium replacement are double those for the rubidium replacement is truly remarkable, in every group investigated, while the ammonium replacement approaches in effect the caesium interchange. This will be clearly apparent from the following table showing the average and maximum angular changes for the nickel group of double selenates:

Replacement.	Average Change.	Maximum Change.
K by Rb . . . . .	23'	57'
K by Cs . . . . .	47	119
K by $NH_4$ . . . . .	45	110

If there had been some disturbance of the structure, such as would be provoked by the insertion of additional layers, one would have expected much more disturbance of the interfacial angles than this, even had the type of symmetry been left unaffected (which would have been improbable). Hence, there was every reason to surmise that the internal structural dimensions also had suffered no crucial change, and that they were faithfully indicated by the topic axial ratios. Now, when we make the comparison of these ratios and of the molecular volumes of the four salts we find that the values for the ammonium salt are almost identical with those of the rubidium salt. This will be clear from an inspection of the table on page 641 or 703. From this, and from similar relationships which have been observed by the author for the ammonium and rubidium salts of every group of double sulphates and selenates, it has been concluded that the structures of the ammonium and rubidium salts of these series are not only similar but practically "isostructural." If they could be imagined as shadows (non-material) and one such ghostly space-lattice could be moved over and through the other consequently without interference, it could be brought into approximately actual identity with that other.

Before proceeding to indicate the great significance of this, it should be stated that there is further independent information available to show that it is a real fact. It has been shown by the author that the ammonium and rubidium salts, of the two great rhombic and monoclinic isomorphous series studied in detail, exhibit a remarkable facility for the formation of mixed crystals.<sup>1</sup> The analogous potassium and rubidium

<sup>1</sup> Indeed, the rhombic form of ammonium selenate (which salt usually crystallises

salts, or the rubidium and caesium salts, show very little such tendency to crystallise together, and the potassium and caesium salts, which differ most in molecular volume and topic axial ratios, practically never crystallise together. G. Wulff<sup>1</sup> has also independently discovered the fact as regards ammonium and rubidium sulphates, obtaining perfect mixed crystals of these salts, while he found potassium and caesium sulphates to be totally immiscible, which he attributes to the great difference in their molecular volumes; he, too, obtained only very imperfect mixed crystals of either ammonium or rubidium sulphate with potassium or caesium sulphate. Further, T. V. Barker has shown,<sup>2</sup> in a beautiful series of researches, that the facility for forming overgrowth crystals or parallel growths of one salt of an isomorphous series on another is dependent on congruency of structure, as indicated by closeness of molecular volume and topic axial ratios; and that the rubidium and ammonium salts of the same acid (sulphates, chromates, and perchlorates were studied) exhibit the property *par excellence*, while the corresponding potassium and caesium salts form no such over- or parallel growths at all, or do so to a very low minimum extent.

Hence, we are compelled to conclude, the evidence being overwhelming, that the crystal structures of ammonium and rubidium sulphates (and of the analogous double sulphates or selenates containing these two alkali bases and the same dyad-acting metal) are almost identical, isostructural, that is, congruent to a remarkable degree. But this conclusion obviously means that the two atoms of rubidium are replaced by the 10 atoms of  $2\text{NH}_4$  without any opening up of the structure. In other words, the structure must either be already sufficiently open to permit of the insertion of the eight additional atoms, or the volume of the two ammonium radicle groups must be approximately the same as that occupied by the two rubidium atoms.

It will be obvious that this conclusion has an important bearing on the valency volume theory of Barlow and Pope,<sup>3</sup> now under discussion. No adequate explanation or serious attempt at such has been given by them of the difficulty. The very essence of their theory is that each valency in a given compound has the same volume, and that, therefore, the atomic volumes of combined elements are directly proportional to their valencies. The theory is, of course, entirely inconsistent with Kopp's idea of molecular volume. Thus, in  $\text{K}_2\text{SO}_4$  the two monadic potassium atoms are each supposed to occupy unit volume, the four dyadic oxygen atoms each to occupy two volumes, and the sulphur atom is considered, somewhat arbitrarily, to be also only dyadic and to occupy two volumes; the total

K O S

volume would thus be  $2+8+2=12$ . Similarly, the two rubidium and caesium atoms in the isomorphous salts would occupy the same relative

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exceptionally in a monoclinic form, being dimorphous) isomorphous with potassium, rubidium, and caesium selenates, has only hitherto been obtained by the author in large crystals when admixed with more or less rubidium selenate.

<sup>1</sup> *Zeitschr. für Kryst. Min.*, 1906, 42, 558.

<sup>2</sup> *Journ. Chem. Soc.*, 1906, 89, 1120; and *Mineralog. Mag.*, 1907, 14, 235; and 1908, 15, 42.

<sup>3</sup> *Ibid.*, 1906, 89, 1675; 1907, 91, 1150; 1908, 93, 1528.



volumes of two out of twelve; and the relative total volumes, as expressed directionally by the "equivalence parameters" employed by Barlow and Pope (who discard topic axial ratios), are also practically identical for the three salts. The theory does not account at all for the considerable increase in molecular volume on passing from the potassium salt through the rubidium to the caesium salt, corresponding to the very considerable rise (more than tripling) in the atomic weight of the metal, to the tripling of the atomic number, and to the increasing complexity of the atom itself, and indeed ignores it.

In their very first paper Barlow and Pope take<sup>1</sup> the case of these sulphates and selenates of potassium, rubidium, and caesium as an example of the working of their theory; they omit all reference to ammonium sulphate, however. They employ the author's experimental data, and give a table which is reproduced below, of the "equivalence parameters"  $x$ ,  $y$ ,  $z$ , which they calculate like topic axial ratios, except that they use the sum of the valencies, the valency volume  $W$ , instead of the author's molecular volume  $V$ , together with the author's crystal-axial ratios. It will appear from this table that any one and the same parameter for the three different salts of each group (sulphate or selenate) remains almost unaltered. The average difference shown by any one of the three para-

BARLOW AND POPE'S EQUIVALENCE PARAMETERS FOR  $R_2\overset{S}{\text{Se}}\text{O}_4$ .

	V.	W.	$x$ : $y$ : $z$ .
$\text{K}_2\text{SO}_4$ . . .	64.91	12	2.2109 : 2.1977 : 2.8463
$\text{Rb}_2\text{SO}_4$ . . .	73.34	12	2.2049 : 2.1899 : 2.8648
$\text{Cs}_2\text{SO}_4$ . . .	84.58	12	2.2003 : 2.1826 : 2.8777
$\text{K}_2\text{SeO}_4$ . . .	71.67	12	2.2207 : 2.2083 : 2.8204
$\text{Rb}_2\text{SeO}_4$ . . .	79.94	12	2.2147 : 2.1957 : 2.8412
$\text{Cs}_2\text{SeO}_4$ . . .	91.09	12	2.2112 : 2.1900 : 2.8524

eters for the two extreme (potassium and caesium) salts of each group is less than 1 per cent. Indeed, the maximum difference over the whole six salts, including that due to the replacement of sulphur by selenium, is only just 2 per cent. for the third parameter, and it is only 1 per cent. for the first parameter, and 1.3 per cent. for the second parameter. The real directional changes, however, as shown by the topic axial ratios, (table on p. 641 or 703), are 10 per cent. in either group, and 12 per cent. over the two groups (from  $\text{K}_2\text{SO}_4$  to  $\text{Cs}_2\text{SeO}_4$ ), while the real change in total volume is as much as one-third. In connection with this table, Barlow and Pope say specifically that the interchangeable elements of the same group of the periodic system are represented by spheres of atomic influence of nearly the same size as compared with the sphere volumes of other constituents.

Now, it will be at once apparent that if we replace  $\text{Rb}_2$  by  $2\text{NH}_4$  we shall, according to the valency volume theory, be replacing two unit volumes by 10 atoms of volume 14, taking nitrogen at its lower triadic

<sup>1</sup> *Journ. Chem. Soc.*, 1906, 89, 1724.

valency, and, therefore, as of volume 3, and hydrogen as 1, the whole salt then having a volume of 24; if nitrogen be pentadic, as is more logical and more in accordance with chemical facts, clearly four more units of volume must be added, making 28. That is, according to the valency volume theory, and on the lower estimate, we double the volume, from 12 to 24, on passing from rubidium sulphate to ammonium sulphate. This, however, has been shown by the author not to occur, but that, on the contrary, the volumes of the ammonium and rubidium salts are almost identical and closely isostructural.

There is now much evidence, from the work of other investigators, that the valency volume theory can no longer be entertained. It has always appeared to the author to be unlikely to represent the truth. Until, however, definite experimental evidence of a decisive character was forthcoming, such as that now afforded by the X-ray analysis, the author has not felt justified in expressing his views. It appeared most unlikely that a theory could be correct which does not admit the undoubted very considerable increase in volume (one-third of its bulk) which occurs on replacing potassium in potassium sulphate by caesium, the equivalence parameters of Barlow and Pope showing an almost negligible change, as already pointed out in connection with the table of these parameters just given. A considerable increase was in any case to be expected, corresponding to the increase in complexity and in material content of the atom (probably by the addition of further rings, shells, or other distributions of negative electrons, in accordance with Moseley's law), indicated by the rise in atomic weight from 38.85 to 131.9, and of the atomic number from 19 to 55. Yet, while taking practically no note of this, the theory asserts that the volume of the oxygen atom, of the low atomic weight 16 and atomic number 8, is twice as great as that of the caesium atom, or whatever alkali atom is present in combination with the oxygen.

Moreover, it has been possible to put forward the theory only by the aid of what cannot be called anything else than quite unwarrantable arithmetical manipulation of the crystal-axial ratios, the arbitrary dividing or multiplying of certain ratios by various numbers to suit the exigencies of the theory. This manipulation has been defended by the authors of the theory and is maintained and used extensively by Barlow in the very latest memoir on the subject,<sup>1</sup> as justifiable on the ground that a certain amount of arbitrariness exists in the choice of the crystal axial planes. It is argued that planes corresponding to the manipulated ratios may be considered equally as valid for axial planes as those chosen by the crystallographer who measured the crystals. This contention, however plausible, is not to be substantiated. There is always some good reason for the choice of particular planes for axial planes, such as the fact that these planes were generally the vastly predominating ones developed as faces, and were parallel or otherwise definitely related to the cleavage planes discovered. Moreover, Fedorov<sup>2</sup> has recently indicated means, as

<sup>1</sup> *Mineralog. Mag.*, 1916, 17, 314.

<sup>2</sup> E. S. Fedorov, *Crystallochemical Analysis* (Russian), 1914; *Zeitschr. für Kryst. Min.*, 1913, 53, 337; 1914, 54, 17.

described earlier in this chapter, by which the correct setting of a crystal, which involves the proper choice of axial planes, can be checked and in doubtful cases determined, so that there is no longer any excuse for the incorrect choice of these fundamental planes. In general, although there are exceptions such as that in the case of the double sulphates and selenates pointed out by the author, the decision afforded by Fedorov's method is given in favour of simplicity and low indices for the other planes developed on the crystal. Barker,<sup>1</sup> who has made a special study of Fedorov's method, and has worked in his laboratory at Petrograd, has shown, however, in typical cases taken from among those put forward by Barlow and Pope, that the new crystal elements arrived at by their manipulations lead in general to greater complexity of the indices of the other faces, in some cases, indeed, grotesquely so. This indicates the inherent improbability that the manipulation was justifiable. Barker has further shown that ninety of the hundred examples put forward by the supporters of the theory are tainted with this arbitrary and unwarrantable manipulation of the axial ratios. Further, that on the most generous basis not more than five cases out of the hundred can in any sense be regarded as being in consonance with it, and not one of them actually demands the theory as the sole or even the best explanation.

A very important contribution to the subject has also been made by Prof. Theodore Richards (Harvard),<sup>2</sup> in two memoirs dealing with the subject which he has made his own, the compressibility of atoms. He shows that the valency volume theory is directly opposed to the results of his investigations, and that it leads to extraordinary and highly improbable conclusions. Richards, indeed, can find no plausible reason why each valency in a given compound should have the same volume. He gives one remarkable illustration of the impossible situation in which the theory lands its supporters, that of the relationship between benzene and tetrabromobenzene. There is no reason why all the remaining carbon and hydrogen atoms in benzene should nearly double their volume when four atoms of bromine are substituted for hydrogen, as the valency volume theory demands. The more reasonable explanation, as all Kopp's work shows, is that the atomic volume of bromine in combination is much larger than that of hydrogen, as we should obviously expect it to be from its much greater atomic complexity; but they are the same, each of unit volume, according to the valency volume theory.

Richards shows, moreover, that the most striking argument advanced by Barlow and Pope, derived from the results of Le Bas for the molecular volumes of the liquids of normal paraffins just above their melting points, is an entire fallacy. He shows that (quite apart from the fact that these are liquids and not solids, and that an arbitrary temperature is chosen for the comparison) the agreement between the molecular volumes and the volumes calculated on the Barlow-Pope basis of vol. C=4 vol. H, is no better than would occur on almost any other assumption. For instance, if the volume of the carbon be taken as twice that of the hydrogen, the

<sup>1</sup> *Journ. Chem. Soc.*, 1915, 107, 744.

<sup>2</sup> *Journ. Amer. Chem. Soc.*, 1913, 35, 381; 1914, 36, 1686.



agreement is practically as good, and if carbon be taken as five times hydrogen, the agreement is twice as good.

The memoirs of Richards are particularly interesting, as they deal specifically with the isomorphism of the ammonium and potassium salts. He considers its explanation quite beyond the reach of the valency volume theory, which gives to ammonium nine volumes (according to Richards, but seven according to Barlow and Pope, who take nitrogen arbitrarily as triadic instead of pentadic), but to potassium only one volume. He finds it hard to see how any sort of analogous symmetry could be constructed in the two cases under the circumstances. The work on compressibility of atoms, however, suggests that the five atoms making up the radicle  $\text{NH}_4$  possess together about the same volume as the potassium (or, better still, according to the author's work, rubidium) atom, and are compressed by their mutual affinities into a shape not unlike that occupied by the compressed and distorted alkali metallic atom. Richards finally concludes that the doctrine of valency volume is irreconcilable with a broader view of the nature of solids and liquids and the mechanism of chemical change.

Barlow and Pope replied <sup>1</sup> to the first paper of Richards, but after the second they published only a short note, <sup>2</sup> in which the statement was made that a weighty reason rendered further discussion at that time (August 1914) futile, namely, that "during the last year or two a method for the practical determination of crystal structure has been developed by Laue, and W. H. and W. L. Bragg, which gives every promise of ultimately leading to very precise information concerning the arrangement of the atoms in a crystalline structure. . . . Further discussion may well be postponed until the important developments which are promised have had time to mature." This time would appear to have arrived in the year 1916. For in the preceding year it had appeared to the author that the X-ray spectrometric analysis of crystals had been brought to such perfection by Sir W. H. and Prof. W. L. Bragg, <sup>3</sup> that a new method of attack was available, which would afford a crucial test of the validity, on the one hand, of the author's conclusions based on his experimental results and the conceptions of molecular volume and topic axial ratios, and, on the other hand, of the valency volume theory of Barlow and Pope. The author therefore suggested to Sir W. H. Bragg that an X-ray analysis of the rhombic alkali sulphates and selenates would prove of extreme value, and Sir William happily concurring he arranged in January 1916 for such an analysis to be carried out in his laboratory, with crystals supplied by the author, many of them being the actual crystals employed in the author's published investigations. The work was carried out by Prof. A. Ogg and Mr. F. Lloyd Hopwood, and has been described in the preceding chapter on "X-rays and Crystal Structure," pages 700 to 704. The results have proved conclusively that the ammonium and rubidium salts are, indeed, practically iso-structural, the actual dimensions (absolute volumes and distances in space) of the space-lattice elementary cells having been

<sup>1</sup> *Journ. Amer. Chem. Soc.*, 1914, 36, 1675.

<sup>2</sup> *Ibid.*, 1914, 36, 1694.

<sup>3</sup> *X-rays and Crystal Structure*, G. Bell & Sons, 1915, 2nd edition, 1916.

measured, and found to be precisely as closely identical as is indicated relatively by the molecular volumes and the topic axial ratios. The dimensions for the potassium and cesium salts, moreover, are found to be considerably different, just as much so, in fact, as is suggested by the molecular volumes and topic axial ratios for those salts. The actual directional dimensions in space, as measured directly by the X-ray spectrometer, are wonderfully close to the author's values for the topic axial ratios. These latter constants, therefore, are both justified and verified. On the other hand, there can be no other conclusion than that the valency volume theory is not based on fact, and is fallacious.

In view of the possibility of the suggestion being put forward that although there are 24 valency volumes in  $(\text{NH}_4)_2\text{SO}_4$  and only 12 in  $\text{Rb}_2\text{SO}_4$ , the actual spheres of atomic influence in the former are on a smaller scale than in the latter, such as affords in the total the same volume for the two salts, it may be said that such an assumption would be even more arbitrary than that denounced by Richards in the case of tetrabromobenzene; or than that which Barlow and Pope made concerning the replacement of K in KI by  $\text{NH}_4$  (according to which the volume of the iodine suffers a shrinkage of five-sevenths of the bulk which it occupies in the potassium salt), and which has been shown by Barker<sup>1</sup> to be most unreasonable.

In the opening words of his last memoir, communicated to the Royal Society only very shortly before his lamented demise, the late Sir William Ramsay<sup>2</sup> stated: "It is now almost universally acknowledged that the valency of an element is due to its being associated with one or more electrons." This idea as to the nature of valency, which assigns a practical meaning, that of an attaching electron or electrons—the oscillating valency-electron or, more probably, simply the electrons of the outer shell (possibly more or less fixed in position)—to the older idea of a "bond," is one which is rapidly developing from the great progress now being made in our knowledge of the nature of the atom, due very largely to the researches of Sir J. J. Thomson, Sir E. Rutherford, van den Broek, Bohr, Moseley, and still more recently Lewis, Langmuir, and W. L. Bragg, as described in the last few pages of the preceding chapter and in Chapter XXXV. Indeed, it is a natural corollary to the beautiful structure of the atom, as we now know it from these researches; and especially from the revelation in the work of Moseley<sup>3</sup> (unhappily his last) of the important function of the atomic number in corresponding to the positive nuclear charge, and thereby determining the number of negative satellite electrons in the electrically stable atom. Valency, therefore, would appear to be due to a cause quite incompatible with the volume effects assumed by Pope and Barlow.

**Moseley's Law, and its Explanation of Crystallographic Progression.**—This concluding chapter of Part II. may, therefore, fittingly terminate with a brief statement as to Moseley's results. For, together with the Bragg law of atomic diameters explained in the last chapter, they afford an admirable explanation of, and the key to, the progression of the

<sup>1</sup> *Journ. Chem. Soc.*, 1912, 101, 2496.

<sup>2</sup> *Roy. Soc. Proc.*, 1916, 92, 451.

<sup>3</sup> Killed at Suvla Bay, Dardanelles, 1915.



crystallographic properties with atomic weight and atomic number, the law concerning which, valid for all the groups of isomorphous salts which have been investigated by the author, is probably both the most interesting and the most important outcome of the author's own researches.

With equal validity "atomic number" can be substituted for "atomic weight" in the statement of the author's law of progression of the crystallographic properties. For the differences between potassium, rubidium, and caesium are similarly related as regards both functions, rubidium standing half-way between potassium and caesium in both respects, as will be clear from the following comparison :

	K.	Rb - K.	Rb.	Cs - Rb.	Cs.	Cs - K.
Atomic weights .	38.85	46	84.9	47	131.9	$93 = 2 \times 46.5$
Atomic numbers .	19	18	37	18	55	$36 = 2 \times 18$

The differences between K and Rb, and Rb and Cs, are thus equal for both constants, namely, 46 or 47 in atomic weight and 18 in atomic number, and the difference between the two extreme members of the family group, potassium and caesium, is double as much, namely, 93 for atomic weight and 36 for atomic number.

The atomic number, the sequence number of the element, when all the elements are arranged in order of ascending atomic weight in the periodic table (see page 768 in the next chapter), has acquired great significance from the work of Moseley, who in two memoirs on "The High Frequency Spectra of the Elements" <sup>1</sup> has shown definitely and experimentally that the atomic number represents the value of the charge N of positive electricity on the atomic nucleus. For we already knew from the work of Sir J. J. Thomson, Sir E. Rutherford, Barkla, van den Broek, and Bohr, sufficient concerning the structure of the atom to render it certain that there is an inner positively charged nucleus, surrounded by a number of negatively charged electrons approximately equal to half the atomic weight, and together equivalent electrically to the positive charge on the nucleus; and van den Broek and Bohr had suggested that the nuclear charge N would prove to be equal to the atomic number. Now N increases from the atom of one element to the atom of the next in the periodic table always by a single positive unit, the positive charge carried by the nucleus being in all cases an integral multiple of the charge on the hydrogen nucleus; thus, for instance, while hydrogen has one nuclear charge, helium has two such charges, and lithium three. The decisive work of Moseley, in his last research, has been to show (a) that the X-ray spectra of the line series known as K are derived from the innermost ring of electrons, while those of the L series are derived from electrons farther from the centre of the atom; (b) that the frequency of the spectra is proportional to  $(N - a)^2$  where  $a$  is a

<sup>1</sup> *Phil. Mag.*, series 6, 1913, 26, 1024; 1914, 27, 703; see also "Obituary Notice," by Sir E. Rutherford, *Roy. Soc. Proc.*, A, 1917, 93, xxv.



constant dependent on the line series used, its value being 1 for the K series and 7.4 for the L series (for the  $\alpha$  line in each case); and (c) that N itself, the nuclear charge, is none other than the atomic number.

The truth of Moseley's law has recently (1920) been proved by direct determination of the positive electric charges on the nuclei of the atoms of copper, silver, and platinum, by J. Chadwick.<sup>1</sup> The method depended on the scattering of  $\alpha$ -particles, and an incidental highly interesting result was the observation that the law of inverse squares holds for the force between the nucleus and the  $\alpha$ -particle in the passage of the latter round or in the neighbourhood of the nucleus for a range of  $10^{-11}$  cm. around it, in fact, right up to the K-ring or shell of electrons. The positive charges actually found were 77.4 for platinum, 46.3 for silver, and 29.3 for copper; the atomic numbers of the three elements are 78, 47, and 29. Thus Moseley's law is most satisfactorily confirmed by direct experiment.

The atomic number, or element sequence number, is thus a very important factor in the constitution of the atom, and it is therefore very likely to be a correspondingly governing factor in determining the relative properties of a eutropically isomorphous series of salts, formed by the interchange of atoms of elements of the same family group of the periodic classification, such as the three alkali metals, which differ regularly from one another in position by two whole horizontal rows of elements at a time (18 elements). Indeed, the work of Moseley shows clearly that the properties of the atom are better defined by the atomic number than by the atomic weight. It has always been difficult to see why mere atomic weight should wield the influence which has been pointed out by the author, and the author has been careful to emphasise that he regarded atomic weight as only another progressively changing property, very convenient, however, for purposes of reference as regards the chemical position of the element, but equally with all the other progressing properties dependent on some hitherto unknown fundamental difference in the chemical elementary atoms. This fundamental difference is now proved by Moseley to be the positive electric charge on the atomic nucleus, and as this determines the atomic electronic complexity (as regards the number of the surrounding negative electrons) and the atomic number is its measure, there is a logical reason why increase in the atomic number, in the case of a regularly ascending series of family group elements, should be effective in similarly progressively modifying the crystallographic and physical properties of isomorphous salts containing those elements. Moreover, the fact that W. L. Bragg has shown that a similar progression occurs with respect to the atomic diameters of potassium, rubidium, and caesium, which are respectively 4.15, 4.50, and 4.75—these three alkali metals occupying the sharp maxima of the curve of atomic diameter given in Fig. 584a on page 712—assists still further in explaining why such a crystallographic progression should occur, not only with respect to the structural dimensions but also with regard to the physical properties.

<sup>1</sup> *Phil. Mag.*, 1920, 40, 734.

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<sup>1</sup> The spelling of the name of this author with the modern German ö was adopted in the Report of the British Association Committee on the Structure of Crystals; it is spelt with the older oe, namely, Schoenflies, in his own books and memoirs.



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